Department of Civil Engineering

Removal of Bromide from Drinking Water Sources using Silver Impregnated Activated Carbon (SIAC): Understanding Br-SIAC Interactions

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Declaration

To the best of my knowledge and belief this thesis contains no material previously published by any other person except where due acknowledgment has been made.

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Abstract

Elevated concentrations of naturally occurring bromide in drinking source waters can cause a multitude of water quality problems. When water is disinfected by chlorine, bromide is rapidly converted to hypobromous acid (HOBr) which reacts in an analogous way to chlorine (HOCl). However, reactions involving HOBr are generally several orders of magnitude faster than those of HOCl. In addition, the reactivities of brominated DBPs (Br-DBPs) are generally also higher than those of the chlorinated analogues (Cl-DBPs), which makes them more physiologically active and more toxic. Due to its complex interaction with chlorine, bromide can be considered as a catalyst in many of the reactions involving chlorine in drinking water supply systems and therefore it effectively increases the rates of many of these reactions. In addition to the formation of disinfection by-products, bromide in source water causes water quality problems including increased disinfectant loss and higher concentrations of odorous brominated compounds. Conversely, the presence of bromide can also be advantageous e.g., HOBr can expedite the oxidation of manganese (II) to MnO_2 which is removed by a filtration process and it can increase the rate of iodide oxidation to iodate minimising the formation of toxic I-DBPs. However, Br-DBPs (organic bromine), typically measured as adsorbable organic bromine (AOBr), have recently been reported as the dominant halogenated species in chlorinated ground- and surface-raw waters containing high concentrations of bromide. In addition, during disinfection with ozone, bromide can form bromate, a regulated DBP and suspected carcinogen. Bromide is oxidised to bromate via a complex series of mechanisms and although its formation may be minimised by pH control the avoidance of bromate formation is most effective at low bromide concentrations. For the multitude of reasons above, it is desirable to remove bromide prior to the final disinfection step. Despite considerable efforts to develop new methods for bromide removal from drinking water, high-cost reverse osmosis is still the only practical method for producing water with low concentrations of bromide ions in finished water. There is, therefore, a requirement for a simple and robust method for selective removal of bromide that can be readily retrofitted to existing conventional water treatment processes for minimal capital and operational cost.

Silver-impregnated activated carbon (SIAC) has shown excellent potential as a viable alternative to selective removal of bromide during drinking water treatment (Watson et al. 2016; Chen et al. 2017). The main focus of this study, therefore, was to investigate the capacity of several SIAC adsorbents to remove bromide from drinking source waters under realistic conditions. Several factors determining the practicality of the use of SIAC for selective removal of bromide were investigated. In Chapter Three, a feasibility study was carried to systematically examine SIAC adsorption affinity, both for bromide and for natural organic matter (NOM) in synthetic and real water matrices. New approaches to minimise silver leaching and studies to gain a better understanding of the mechanisms of silver leaching from SIAC are described in Chapter Four. In Chapter Five, the observation of a distinguishable difference in bromide removal for NOM extracts with various chemical compositions and molecular weight distributions is discussed. Chapter Six provides the overall conclusions from this thesis which lead to some recommendations for further studies.

The discussion in Chapter Three describes testing of three types of commercially available SIAC and one type of granular activated carbon (GAC) without silver impregnation for their capacity to remove bromide from samples of both synthetic and real water. Comparison of the bromide removal capacities of the different types of SIAC and the GAC confirmed previous studies showing that the incorporation of silver into the activated carbon matrix is highly efficient in removing bromide, although substantial variation was observed between the different materials tested. The Norit SIAC, which performed better than the other adsorbents tested, removing up to 95% of initial bromide (12.5 μM), was studied in more detail for its capacity to adsorb bromide during three consecutive adsorption tests. In the first of three consecutive tests, up to 95% of initial bromide was removed, but 40% lower bromide removal capacity (15 μmol/g) was observed during the second and third tests. This reduction in bromide removal capacity was attributed to the decrease in Ag^+ incorporated into Norit SIAC that was available react with bromide. Kinetics studies revealed more than 66% decrease in dissolved bromide was observed after the first 30 minutes ($[Br^-]_{t=30min}$ = 4.2 μmol/g) which fitted well with a first-order rate model. As the adsorption continued to the second stage (30 – 120 min), the difference (overestimation) between model and experimental bromide removal data was attributed to the change in intrinsic mechanism (surface co-precipitation) and the

consequent reduction of available adsorption sites in SIAC. To assess the impact of dissolved organic matter (DOC) on the bromide removal capacity of Norit SIAC, tannic and gallic acid organic model compounds (3.6 mgC/L) and various concentrations of Suwannee River Humic (SRHA) and Fulvic (SRFA) acids (1, 2 and 4 mgC/L) were added to water containing bromide. Results showed that the rate of bromide removal in the control, in the absence of organic matter, was faster within the first 30 minutes compared to samples that contained dissolved organics. Overall, this study showed that the presence of organic compounds altered the removal of bromide, such that the kinetics of removal were slower, but that the overall bromide removal capacity remained unchanged after agitating for a longer contact time (180 minutes).

Chapter Four focused on the evaluation of one type of commercially available SIAC for its ability to remove bromide while minimising silver leaching from the material. Both synthetic and real water matrices were tested. The study results suggested that the extent of silver incorporation is not the only factor determining the efficiency of SIAC for bromide removal applications. Depending on solution pH, it was found that changing the surface charge properties of SIAC, as measured by the point of zero charge pH (pH_{PZC}), can also result in additional bromide removal while minimising the extent of silver leaching. In fact, increasing the solution pH would reduce the negative surface charge and at a high pH silver leaching is minimised. Therefore, to mitigate silver leaching, the SIAC was preconditioned at high pH (pH 10.4). To better understand the mechanism of silver leaching from the SIAC, eight preconditioning environments, i.e. variable pH and ionic strength (IS) were tested for a fixed amount of SIAC and two preconditioning environments were selected for a more detailed investigation. Experiments carried out in synthetic water showed that preconditioning at pH 10.4 did not deteriorate the capacity of SIAC to remove bromide, but significantly decreased the release of silver in the form of ionic silver (Ag^+), silver bromide (AgBr) and silver chloride (AgCl) from 40% for the pristine to 3% for the treated SIAC. Due to its superior silver leaching properties, these results suggested that preconditioned SIAC has the potential to be an effective method for bromide removal with minimised silver leaching from drinking source water in a long-term field application.

Experiments discussed in Chapter Five were carried out to further investigate the apparently conflicting hypotheses regarding the interpretation of NOM effects on the bromide removal capacity of silver-impregnated adsorbents. Previous studies had reported a reduced bromide removal efficiency from surface waters containing 3.4 and 1.4 mgC/L of NOM due to blockage of pores, caused by the physisorption of the smaller fractions of NOM, along with a direct complexation interaction of negatively charged NOM molecules with Ag^+ sites. Another study showed that the presence of 12 mgC/L of Suwannee River NOM (SRNOM) did not significantly deteriorate the bromide removal efficiency of SIAC, where the bromide removal was above 90% across the sample matrices. The dominant mechanism for interplaying of NOM and SIAC were then explained by hydrophobic interactions between them, while the interactions of hydrophilic sites of NOM molecules with the Ag^+ sites appearing to be unimportant.

These apparently conflicting outcomes on the impact of NOM on the bromide removal capacity of silver-impregnated activated carbon were therefore further investigated. For this purpose, a commercially available SIAC was used to evaluate the impact of various NOM extracts with different physiochemical characteristics ($2.51 \leq SUVA_{254} \leq 5.16$) on the extent of bromide removal. For all types of NOM extracts, increasing the SIAC dosage from 0.5 to 2 g/L significantly improved both the bromide and NOM removal. This could be due to the increase of available active sites on the SIAC that reacted with both bromide and NOM molecules. All types of NOM extracts were shown to reduce the bromide removal through SIAC, but a distinguishable difference was observed in terms of the effect of each NOM extract on bromide removal. The chemical composition of NOM appeared to play an important role, e.g. sulphur–rich NOM more significantly decreased bromide removal efficiency, whereas NOM removal was improved. Additionally, nitrogen-rich NOM with high affinity towards Ag^+ sites on SIAC resulted in the highest extent of silver leaching into solution. The findings obtained from studies using NOM extracts were supported by experiments using small model compounds including glycine (nitrogen-rich), thioglycolic acid (sulphur–rich) and sodium propionate (control). The presence of thioglycolic acid lowered the bromide removal efficiency from above 95% to 60%, possibly due to the inactivation of SIAC adsorption sites by direct complexation Ag^+ with electron donating sulfhydryl groups. In contrast, the presence of glycine did not significantly

reduce the bromide removal capacity, but the extent of silver leaching was increased. The solubility of silver bromide (5.2×10^{-13}) is significantly lower than that of silver-glycine (1.28×10^{-7}) and therefore, the anion exchange of glycine for bromide is expected to occur. As a result, an alternative bromide removal pathway can be considered through glycine complexation dissolution of Ag^+ followed by the bromide-glycine anion exchange reaction. These experiments suggested that in addition to physical characteristics of NOM (e.g. $SUVA_{254}$), its chemical composition also plays an important role in controlling the extent of bromide removal and silver leaching of SIAC.

This thesis sheds light on some of the challenges in the practical implementation of selective removal of bromide during water treatment, prior to final disinfection. The detailed results of SIAC silver leaching stability suggest that commercially available SIAC may not necessarily be directly applicable for bromide removal applications. However, it was shown that this can be remedied to some extent by preconditioning the SIAC prior to use in order to minimise the extent of silver leaching into solution. The study also showed that NOM with high affinity for Ag^+ (e.g. NOM rich in some sulphur or/and nitrogen functionalities) can have different effects on bromide and NOM removal of SIAC. NOM with nitrogen functionalities potentially can increase the extent of silver leaching while bromide removal remained almost unchanged. In the case of NOM with elevated sulphur content, a higher adsorption affinity towards SIAC was observed which consequently resulted in decreases in both the extent of bromide removal and silver leaching from SIAC. In addition, the $SUVA_{254}$ value indicating the extent of aromaticity in NOM molecules, was found to be an important factor affecting the performance of SIAC. The study suggested that SIAC has lower affinity for the adsorption of aromatic (hydrophobic) fractions of NOM, whereas NOM fractions with lower aromaticity and greater hydrophilic character have higher binding capacities and affinities for Ag^+ sites in SIAC. The outcomes of this research can be advantageous for the water industry in terms of reducing bromide-related aesthetic problems (tastes and odours and manganese-related discoloured water events) as well as Br-DBP concentrations. The present study contributes to the current knowledge on the use of SIAC to remove bromide from drinking water. This process has potential to provide the opportunity to use source waters that are presently not utilisable (e.g. due to excessive DBP formation) and to potentially be rendered potable.

In general, the application of low cost methods for minimisation of bromide will lead to decreased formation of disinfection by-products and better control of disinfectant residuals, improving risk management for water utilities.

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List of Abbreviations

AAS	Atomic absorption spectrophotometer
Ag-Aerogel	silver-doped carbon aerogel
Ag-cloth	silver-doped polymeric cloth
AgNPs	silver nanoparticles
Ag_{Total}	total amount of silver leached
Ag–NOM	silver-NOM complex
AgX	silver halide
AOBr	adsorbable organic bromide
AR	analytical reagent
b	Langmuir equilibrium constant
Br-DBP	brominated disinfection by-product
C_0	initial liquid-phase concentration
CDI	capacitive deionization
C_e	equilibrium liquid-phase concentration
Cl-DBP	chlorinated disinfection by-product
C_t	liquid-phase concentration per unit mass of adsorbent
$C_{t,ins}$	liquid-phase concentration read by instrument
Da	Dalton
DBP	disinfection by-product
DC	direct electrical current
DOC	dissolved organic carbon
DOM	dissolved organic matter
EC	enhanced coagulation
ED	electrodialysis
EDR	electrodialysis reversal
GA	gallic acid
GAC	granular activated carbon
GW	groundwater
GWTP	groundwater treatment plant

h	hour
HA	humic acid
IC	ion chromatography
IHSS	international humic substances society
IS	Ionic strength
k	rate constant
K	Freundlich equilibrium constant
K_{sp}	solubility product
LDH	layered double hydroxide
LOD	limit of detection
M_A	mass of adsorbent
MCDI	membrane capacitive deionization
min	minutes
MIEX®	magnetic ion-exchange resin
n	Freundlich equilibrium constant
NF	nanofiltration
NOM	natural organic matter
pH_{PZC}	point of zero charge pH
POE	point-of-entry
POU	point-of-use
q_e	equilibrium solid-phase concentration per unit mass of adsorbent
q_m	Langmuir equilibrium constant
RO	reverse osmosis
S_{BET}	specific surface area
SIAC	silver-impregnated activated carbon
SLPCS	silver-loaded porous carbon sphere
SRDOM	Suwannee River dissolved organic matter
SRFA	Suwannee River fulvic acid
SRHA	Suwannee River humic acid
SUVA	specific ultraviolet absorbance
$SUVA_{254}$	specific ultraviolet absorbance at 254 nm
SW	surface water

t	contact time
TA	tannic acid
THM	trihalomethane
TOC	total organic carbon
UV	ultraviolet
V_L	total volume of solution

Chapter 1

Introduction

1.1 Background and Objectives

Production and distribution of safe, clean and high quality potable water is crucial for prevention of waterborne disease. For successful implementation of this goal, a variety of drinking water treatments are used, with the method of choice dependent upon characteristics of the source water and the water quality requirements for the end-use of the water. Figure 1-1 shows a schematic of the process undertaken at a conventional water treatment plant.

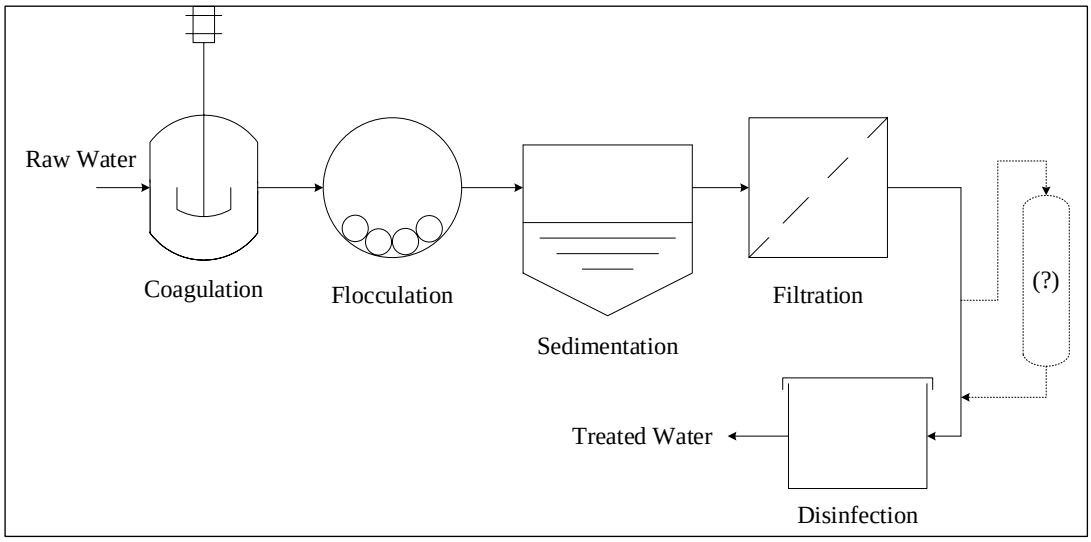


Figure 1-1: A schematic illustration of a conventional water treatment plant

Water entering the treatment plant is subjected to coagulation and flocculation processes in which the negatively charged particles present are converted to neutral flocs upon the addition of positive ions such as aluminium and ferric salts (Bratby 2016). Polyelectrolyte assists the flocculation process and the precipitated flocs are removed via sedimentation basins and sand filtration. An additional size exclusion membrane filtration step (not shown in Figure 1-1) is also considered in some water treatment plants for the further separation of particulates from water. Prior to the water entering the distribution system, it is disinfected to remove pathogens using processes such as chlorination (Cl_2) (Friberg 1956), chloramination (NH_2Cl) (Brodtmann et al. 1979), chlorine dioxide (ClO_2) (Benarde et al. 1965) ozonation (O_3) (Haag et al. 1983), ultraviolet (UV), hydrogen peroxide (H_2O_2), O_3/H_2O_2, O_3/UV and UV/H_2O_2 (Glaze et al. 1987). Recent research, however, has demonstrated that the overall disinfection is substantially affected by the coexistence of some species, in particular bromide (Heeb et al. 2014). As shown in Figure 1-2, reaction of some oxidants with

both bromide and natural organic matter (NOM) results in the formation of toxic chlorinated (ClO_2^-, ClO_3^- and organic chlorinated compounds) and brominated (HOBr, BrO^-, BrO_2^-, BrO_3^- and organic brominated) disinfection by-products (DBPs) (Krasner et al. 2006).

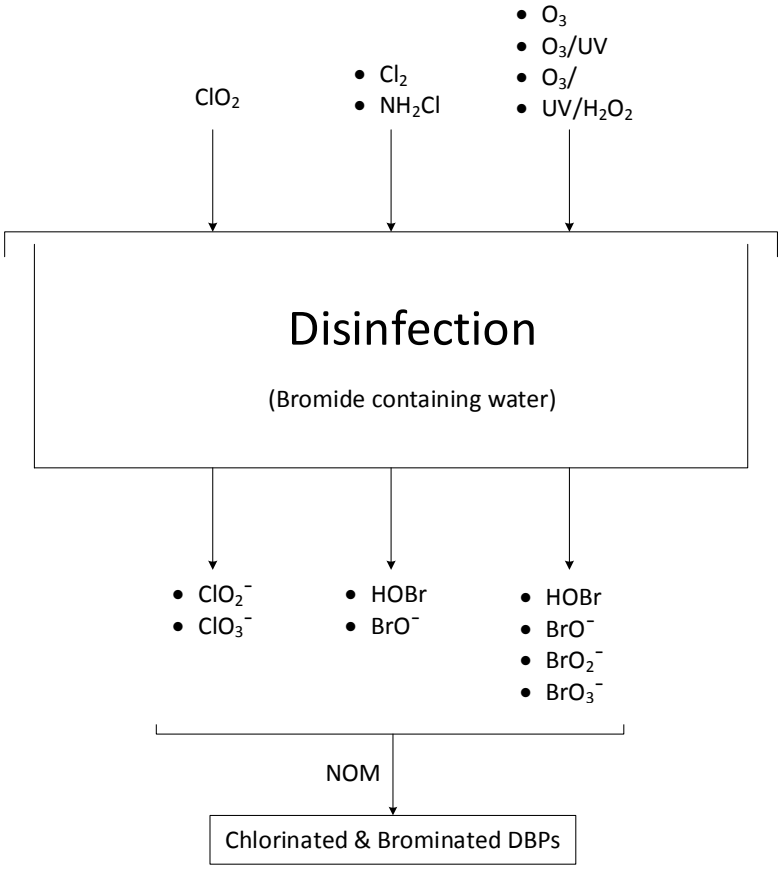


Figure 1-2: An illustration of drinking water disinfection methods and disinfection by-products formed

Therefore, further studies need to focus on effective strategies for the removal of DBP precursors (halides and NOM) prior to the application of disinfection processes (Sedlak et al. 2011). This proposed sidestep is distinguished in Figure 1-1 with dotted lines and a question mark.

There have been major advances in dealing with NOM removal from drinking water (Zularisam et al. 2006; Matilainen and Sillanpää 2010; Matilainen et al. 2010; Qi et al. 2012), but progress on halide minimisation has been very limited, specifically in the case of bromide (Watson et al. 2012). Thus, following short review summarise the

available techniques for the uptake of bromide from aqueous systems.

Bromide has long been problematic during the disinfection of drinking water resources and it is therefore desirable to remove this halide prior to the disinfection step. Pressure driven membrane processes such as reverse osmosis (RO) and nanofiltration (NF) have become the most common commercially available methods which can effectively remove halides and NOM simultaneously up to 99.8% (Harrison et al. 2007; Bartels et al. 2009). However, membranes have disadvantages including susceptibility to fouling and scaling, high energy consumption, short lifespan and costly pretreatment processes. These shortcomings, and the fact that these membrane processes actually treat water to a much higher purity than required (i.e. the processes also remove many substances that don't need to be removed), have led to research to develop alternative selective methods for removal of bromide. Recent studies investigating the different processes applied for the selective removal of bromide from the drinking water resources fall into two main categories: electrochemical (Sata 2000; Kimbrough et al. 2002; Wiśniewski et al. 2011; Łakomska et al. 2013) and adsorption techniques (Chitrakar et al. 2008; Chubar 2011; Chubar et al. 2005; Echigo et al. 2007; Gong et al. 2013; Lv et al. 2008; Sánchez-Polo et al. 2006, 2007).

Electrochemistry has widely been examined for the removal of bromide from drinking water sources using various techniques such as electrolysis, electrodialysis (ED), electrodialysis reversal (EDR), capacitive deionization (CDI) and membrane capacitive deionization (MCDI). Electrolysis uses direct electrical current (DC) to generate a chemical reaction (Hale 1918). This process was first employed by Kimbrough and Suffet (2002) for the removal of bromide from drinking water (Kimbrough et al. 2002). The procedure begins with the oxidation of bromide to a mixture of oxidation products such as HOBr, BrO^- and bromine gas then continues to the degassing step where the solution is purged with the carbon dioxide. The principle is that carbon dioxide purging results in a decrease in pH which converts BrO^- to the more volatile HOBr and Br_2 gas (Kimbrough et al. 2002). Despite the potential of the electrolysis method for bromide removal on a bench-scale, its capacity for scale-up has yet to be examined.

ED and EDR are membrane-based deionization processes in which a low voltage DC is applied to the solution, which causes the flow of ions through oppositely charged

permselective ion-exchange membranes. The major advantage of EDR over the conventional ED process is reduced fouling and cleaning of the membrane surface from accumulated species simply through reversing the electrode polarity at regular intervals (Katz 1982). A limited number of ED and EDR case studies investigating bromide removal from water have recently been published. Banasiak and Schäfer reported on approximately 100% removal of bromide ions from a bore water in a lab-scale containing high concentrations of bromide ions (~10 mg/L) using the EDR method where water samples were sourced from northwest of Alice Springs, Northern Territory, Australia (Banasiak et al. 2009). Valero and Arbós (2010) carried out a long-term pilot plan study of EDR by adding up a sidestep EDR to a conventional desalination plant (Valero et al. 2010). They reached a value of 75% bromide removal after a period of 28 months, where source water with a moderate initial concentration of bromide (0.5−1.2 mg/L) was in use. ED/EDR processes have several advantages over other membrane processes such as minimal need for pretreatment, higher water recovery ratio and longer lifespan than RO and NF, but their application is still limited due to the high capital cost and high energy consumption (Strathmann 2010). Additionally, these processes are not selective because they overtreat (remove other ions that don't need to be removed) and the water also needs to be re-buffered (e.g. by the addition of $CaCO_3$) after treatment, resulting in the use of extra resources and energy. The other main drawback of ED/EDR techniques are their inefficiency to remove uncharged natural organic molecules, unlike RO and NF processes (Watson et al. 2012).

CDI is an electrosorption process which is based on adsorption of charged species onto porous electrodes (e.g. carbon aerogel) under the driving force of an electric field (Gabelich et al. 2002). Promising results from this process have been reported by Welgemoed and Schutte using an industrial module for bromide removal from drinking water (Welgemoed et al. 2005). Although they could successfully remove bromide up to 86% in a synthetic water matrix, the bromide removal efficiency decreased to 62% with the use of a real water sample. They concluded that CDI has the potential to replace conventional desalination methods while further complementary studies are still required to improve the electrode sorption capacity.

The MCDI process is an emerging technology which improves the efficiency of the CDI process (Andelman et al. 2004) by increasing the ion selectivity using ion-exchange membranes attached onto the surface of the electrodes (Biesheuvel et al. 2010). However, this process has yet to be employed for bromide removal and its potential application for this purpose is unknown.

Surface adsorption techniques are widely applied in drinking water treatment, normally as a complementary pre- and/or post-treatment step (Ali et al. 2006; Watson et al. 2012). Ion-exchange resins (Echigo et al. 2007; Hsu et al. 2010), aluminum chloride salt (Ge et al. 2007, 2008), mixed metal hydrous oxides (Chubar et al. 2005; Chubar 2011) and layered double hydroxides (Echigo et al. 2007; Chitrakar et al. 2008; Lv et al. 2008) have been proposed as adsorbents for bromide removal. Although carbonaceous materials have conventionally been effective for the sorption of a wide range of contaminants, most published research shows that they have low selectivity for bromide uptake from an aqueous media. To overcome this issue, some researchers have proposed silver impregnation in order to modify the active sites on the surfaces of a variety of adsorbents. For example silver-doped aerogels and silver-activated carbon aerogels (Sánchez-Polo et al. 2006, 2007) and very recently silver-loaded carbon spheres (Gong et al. 2013) were synthesized and tested using bromide containing feedstock. A brief summary of the feasibility assessment of all adsorbents applied to remove bromide is outlined in the following.

Aluminum chloride ($AlCl_3$. $6H_2O$) was first applied by Ge and Zhu as a coagulant for the removal of bromide from drinking water (Ge et al. 2007). Their adsorption study results are interpreted as follows: depending on the presence of NOM and other coexisting anions, the bromide removal efficiency varied between 98.8% and 43.5% in cases where the adsorbent dosage was fixed at 7 mg/L. The authors concluded that the effectiveness of aluminium coagulation for the removal of bromide deteriorated with increasing concentrations of organic and inorganic coexisting anions.

Chubar and colleagues investigated new inorganic ion-exchangers based on Mg–Al and Fe–Al hydrous oxides used for the adsorption of halides from solution (Chubar et al. 2005; Chubar 2011). Ion-exchange resins are among the most frequently used adsorbent for reducing the concentration of either halides or NOM. Singer and

colleagues extensively studied the viability of magnetic ion-exchange resin (MIEX®) in removing NOM and bromide in the presence of competitive anions in drinking water (Boyer et al. 2005; Hsu et al. 2010). They showed that there was a high removal capacity of MIEX resins for NOM and good bromide uptake by virgin resin. However, bromide uptake by used resin in the presence of NOM was generally too low to be practical.

Echigo et al. (2007) examined another type of commercially available ion-exchange resin (Diaion SA10A) in a comparative study with two types of synthesized layered double hydroxides (LDHs) (Echigo et al. 2007). Although carbonate/bicarbonate anions significantly decreased the effectiveness of bromide removal by both types of ion-exchangers, LDH materials functioned more efficiently than ion exchange resin with respect to bromide uptake in the presence of NOM. Many studies in the literature suggest LDHs as an appropriate adsorbent for aquatic systems. Figure 1-3 depicts a schematic of general LDH anionic clays which have the general formula, $[M^{z+}_{1-x} M^{3+}_{x} (OH)_2]^{\zeta+} (X^{n-}_{\zeta/}n).mH_2O$ where z could be either 1 (Li^+) or 2 (Mg^{2+}, Zn^{2+} and Ni^{2+}) and M^{3+} = Al^{3+} and Fe^{3+}.

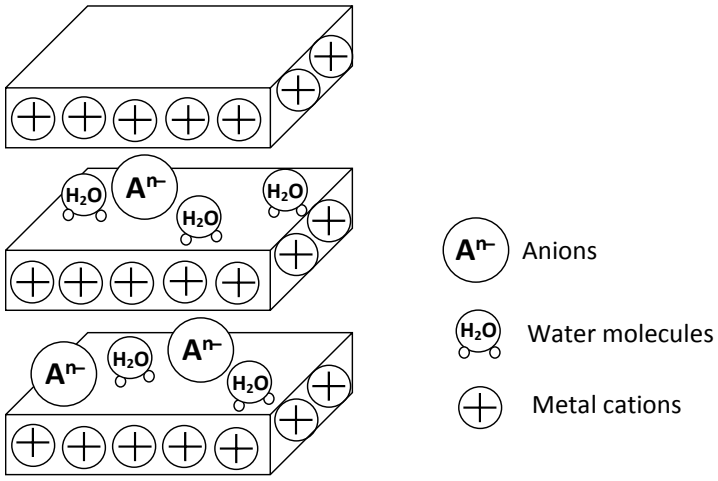


Figure 1-3: Schematic structure of LDHs

These layered materials have recently received considerable attention for their promising textural and chemical properties in water treatment. Good thermal and chemical stability, a flexible interlayer region with high anion exchangeability and high uptake capacity even with apparently low specific surface area are significant

features of LDHs, making them highly selective sorbents in removing organic and inorganic anions from contaminated waters. Investigations on the sorption affinity of LDHs for halides have shown that these materials have high potential to target a particular anion in solution (Lv et al. 2008; Zhou et al. 2011). However, further fundamental studies need to be carried out to systematically identify the factors controlling the anion selectivity mechanism and to determine the viability of LDHs for selective bromide removal.

Hydrogels and xerogels were also found to have capacity for the sorption of both bromide and bromate (BrO_3^-), the main by-product during ozonation. Their selectivity, however, appeared to be very inconsistent as the bromide removal varied substantially from 80% to 9%. Additionally, all adsorption studies were carried out in solutions containing 120 and 200 mg/L bromide which is extremely high compared to the typical bromide concentrations in drinking water plants (<1 mg/L). Silver-doped aerogels are the first carbonaceous materials successfully assessed for bromide removal (Sánchez-Polo et al. 2006, 2007). The results of this research appeared to be promising not only due to the high bromide uptake capacity, but the proposed regeneration process through ammonia solution showed an approximately 100% recovery capacity in three replicates. Further improvement in efficiency was achieved by activation of silver-doped aerogels and silver-activated carbon aerogels in a later study (Sánchez-Polo et al. 2007). Gong et al. (2013) conducted a study on similar materials, preparing highly porous carbon spheres (S_{BET} > 921.3 m^2/g) but the highest bromide removal was only 30% (Gong et al. 2013). However, after loading the carbon spheres with silver nanoparticles the adsorption results significantly increased to just over 90%.

There are, however, some concerns over silver-assisted materials regarding the leaching of silver from the silver halide interface into the bulk solution, leading to contamination of the treated water with traces of silver. Furthermore, silver-carbon adsorbents have been shown to be highly efficient while in contact only with bromide solution without considering the effect of competitive coexisting anions and NOM. It is possible that the porous carbon materials and aerogels would be subject to greater interference in halide removal as they have a relatively high affinity to NOM, due to their organic based structure. In this thesis, the detailed studies of SIAC silver leaching

stability suggest that commercially available SIAC may not necessarily be directly applicable for bromide removal applications. It was shown that this can be remedied to some extent by preconditioning the SIAC prior to use in order to minimise the extent of silver leaching into solution.

Therefore, the factors that were studied in the consideration of silver-incorporated adsorbents for selective removal of bromide, included (a) leaching of silver from the adsorbent into the treated water (b) the kinetics of bromide adsorption and; (c) the impact of competing species such as anions and dissolved organic matter.

1.2 Thesis Overview

This thesis is presented in six chapters. The body of the thesis includes Chapter Two to Five and each chapter consists of a summary of the main subject of the chapter followed by a short introduction and experimental approach. Therefore, some minor repetition of background and method information is occurred.

The main body of this thesis commences with Chapter Two which presents a review of available approaches for the removal of bromide from synthetic and real water matrices. This chapter concludes by identifying the research gaps as the starting point for the further studies in the following chapters.

The main objective of Chapter Three was to better understand the mechanisms of silver leaching from SIAC under typical water treatment conditions in order to develop approaches to minimise silver leaching during bromide removal applications. For this purpose, several factors that govern the practicalities of the use of SIAC for bromide removal, including the kinetics of bromide adsorption and, in particular, the leaching of silver from the SIAC into the treated water, were investigated. The SIAC was first conditioned, in order to modify its surface properties (e.g. reduce silver leaching) based on the SIAC point of zero charge pH. Then, the reaction pathways of the silver and bromide reactions were determined in both pristine and conditioned SIAC. In the last step, the bromide removal and silver leaching efficiency and silver leaching properties of SIAC were examined in a real water sample to identify the most important interferences from components of a natural water matrix.

In Chapter Four, the potential of three types of commercially available SIAC and one type of GAC, without silver impregnation, to reliably remove bromide to low levels (up to 10 µg/L) were investigated. Norit SIAC which had the highest performance was then considered for further evaluation of its Br^- removal and silver leaching properties in the presence and the absence of two natural organic matter (NOM) isolates, Suwannee River Humic Acid and Suwannee River Fulvic Acid. In addition, due to the complexity of NOM mixture, tannic acid (TA) and gallic acid (GA) as NOM surrogates were chosen to systematically examine their adsorption and to determine their interfering effects on Norit SIAC. Finally, a raw water sample collected from a drinking water source in Western Australia was used to assess the bromide removal capacity of Norit SIAC.

Due to the high affinity of NOM molecules towards metallic and dissolved silver, it was expected that NOM would impact both the bromide removal efficiency of SIAC, as well as the silver leaching characteristics. Therefore, in Chapter Five, the main objectives were to examine the effect of NOM isolates with various characteristics on the extent of bromide removal and silver leaching by a commercially available SIAC. It was found that the NOM character significantly affected both bromide removal and silver leaching, with the NOM isolates that contained higher concentrations of sulphur and nitrogen having the greatest impact. These findings were confirmed using simple organic model compounds representing the major classes of NOM used in our experiments. The study showed the importance of NOM chemical composition in its influence on the performance of SIAC in bromide removal applications.

Chapter Six provides the overall conclusions from this thesis followed by a discussion of recommendations for further research.

Chapter 2

Silver-Incorporated Adsorbents for the Removal of Bromide and Consequent Minimisation of Disinfection By-products (DBPs): A Review

2.1 Introduction

Naturally occurring bromide (Br^-) is known to be problematic during the final disinfection step of drinking water treatment (Heeb et al. 2014). Depending on the geochemistry of the materials in which the water has come into contact, the bromide concentrations may vary (Magazinovic et al. 2004). Many drinking water sources in Australia, particularly those in Western Australia, contain elevated concentrations of bromide by world standards (Gruchlik et al. 2015). Based on previously reported classifications, the bromide concentration in natural drinking water supplies can be qualitatively categorised within three risk classes: low (less than 60 μg/L), moderate (ranging from 60 – 500 μg/L) and high (above 500 μg/L) (Ates et al. 2007). A recent local study reported that drinking water sources supplying Perth, the capital city of Western Australia, contain considerably high concentrations of bromide (Table 2-1) (Gruchlik et al. 2015). This table indicates that the bromide concentrations were found to range from 400 μg/L to 8450, where no low risk region for bromide concentration was identified in this survey.

Although water extracted from these sources can be blended to decrease the overall bromide concentrations, this would not be practical in some regional sources where concentrations of bromide in distributed water can exceed 800 μg/L. Treatment and distribution of drinking water containing these high bromide concentrations creates numerous difficulties for water utilities. In bromide-containing water treated with chlorine for the purposes of disinfection, bromide is rapidly converted to hypobromous acid (HOBr) (Kumar et al. 1987), which reacts in an analogous way to chlorine (HOCl), except that reactions involving HOBr are generally several orders of magnitude faster than those of HOCl (Criquet et al. 2012, 2015). Hence, the formation of potentially toxic halogenated disinfection by-products (DBPs) is substantially accelerated and accentuated in chlorinated waters containing bromide. In fact, bromide expedites the chlorine decay in drinking water supply systems. It was also found that the reactivity of brominated compounds are higher than their chlorinated analogous. This means that these compounds tend to be more physiologically active and therefore have both higher toxicities than their chlorinated analogues and are also more organoleptically potent (Flury et al. 1993). In addition to the formation of organic DBPs, bromate (BrO_3^-), another possible human carcinogen, is formed from

bromide when ozone (O_3) is used as the disinfectant (Haag et al. 1983; von Gunten et al. 1994, 1998).

Table 2-1: Concentrations of bromide and their corresponding risk class in some Western Australian raw source waters (GW = groundwater; GWTP = groundwater treatment plant; SW= surface water)(Gruchlik et al. 2015).

Sample	**[Br^-] (µg/L)**	**Bromide Risk class**
North-West Coastal GW	8455	High
Great Southern SW1	847	High
South-East GW	754	High
North-West SW	448	Moderate
South-West SW	400	Moderate
Perth Metro GWTP raw water	743	High
Mid-West eastern GW bore	1460	High
Goldfields GW bore 1	977	High
Goldfields GW bore 2	1385	High
Goldfields GW bore 3	817	High
Goldfields GW bore 4	868	High
Goldfields GW bore 5	717	High
Perth South Coastal GW bore 1	1483	High
Perth South Coastal GW bore 2	479	Moderate
Perth South Coastal GW bore 3	1307	High
Great Southern SW2	561	Moderate
Mid-West western GW bore 1	2249	High
Mid-West western GW bore 2	1908	High
Mid-West western GW bore 3	2807	High
Perth Northern GW bore	567	Moderate
Perth Metro artesian GW	2261	High

There is therefore a requirement for a simple and robust method for selective removal of bromide that can be readily retrofitted to existing conventional water treatment processes for minimal capital and operational cost. A recent study reviewed several types of adsorbents which have been investigated for their capacity to remove bromide from drinking source waters (Watson et al. 2012). Due to the high affinity of halide

ions towards silver, recent research has shown materials which incorporate silver, often within a carbon matrix (e.g. silver-impregnated activated carbon, silver-doped carbon aerogels), can also be a promising alternative for the removal of halides from water (Sánchez-Polo et al. 2006; Watson et al. 2016).

Silver ions (Ag^+) and silver metals (Ag^0) have long been known for their superior antibacterial and biocidal properties in water-related applications. Silver ions derived from silver salts ($AgNO_3$, AgCl), or produced electrolytically, have been investigated for their potential for use as a secondary disinfectant (to reduce levels of chlorine required) in drinking-water supplies (Hwang et al. 2007; Huang et al. 2008; Pathak et al. 2012). Following a review of the literature, Ag^+ has demonstrated efficacy to mitigate biofilm formation in drinking-water distribution systems (Silvestry-Rodriguez et al. 2008). It was also found that Ag^+ can reduce the level of chlorine as a secondary disinfectant (Silvestry-Rodriguez et al. 2007), consequently improving the disinfection of groundwater, wastewater (Cunningham et al. 2008) and the rainwater runoff collected from rooftop harvested rainwater supplies (Nawaz et al. 2012). In combination with copper, the copper/silver ionization process was found to be beneficial for the disinfection of hospital water systems (Cachafeiro et al. 2007) and swimming pool water (Landeen et al. 1989).

The potential of silver metals commonly used in the form of nanosized Ag^0, known as silver nanoparticles (AgNPs), for drinking-water disinfection is currently being extensively explored, principally in conjunction with a substrate to ensure the AgNPs are fixed on the support material. In order to better facilitate the application of AgNPs, a number of media or matrices are reported in the literature as the AgNPs substrate. Polyurethane foam coated with citrate-stabilised AgNPs (Jain et al. 2005) and AgNP-impregnated fibreglass (Nangmenyi et al. 2009), were reported to be promising as an antibacterial surface coating. AgNP-impregnated ceramic filters (Baumgartner et al. 2007; Lv et al. 2009; Brown et al. 2010), silver-containing polymeric microsphere beads (Gangadharan et al. 2010), AgNP-coated polypropylene filters (Heidarpour et al. 2011), AgNP-impregnated papers (Dankovich et al. 2011), AgNP-deposited zeolites (Mpenyana-Monyatsi et al. 2012), AgNP-alginate composites (Lin et al. 2013), were found beneficial for the bacterial removal in point-of-use water treatment. AgNP-treated cryogels (Loo et al. 2013) and biogenic AgNPs, where bacteria are used

as reducing agents for the production of nanosized Ag^0, are widely studied for their superior antibacterial properties in water and wastewater treatment applications.

Two possible bacterial removal pathways that are commonly reported are: (a) the bacteria are killed by Ag^+ released from the substrate (bacteriocidal impact) (Xiu et al. 2011; Li et al. 2012); and/or (b) the bacteria flowing from the substrate are contaminated with silver which prevents their subsequent growth (bacteriostatic impact) (Sondi et al. 2004; Morones et al. 2005). Though Ag^+ is effective in killing pathogenic bacteria, silver also has a strong capacity for the precipitation of halides in solution. Therefore, a form of silver that is immobilised, for example within a filter medium, would be promising for the simultaneous removal of undesirable bromide, where the presence of silver can additionally mitigate bacterial mass growth on the surface of adsorbent. This Chapter reviews the current knowledge of selective bromide removal methods using silver-incorporated materials in water treatment applications.

2.2 Review of Current Research

2.2.1 Silver-Doped Carbon Aerogels (Ag-aerogels)

The first study on the feasibility of application of silver-incorporated materials for the removal of bromide from drinking water sources was conducted by von Gunten and Sánchez-Polo (Sánchez-Polo et al. 2006, 2007). They thoroughly studied the effectiveness of silver-doped carbon aerogels (Ag-aerogels) for the removal of bromide (and iodide) from water samples in batch and column systems (Table 2-2). Ag-aerogels with different pore textures and surface characteristics were successfully fabricated by dissolving the silver salt in a sol-gel process. The maximum adsorption capacity for bromide was 3.01 μmol/g, using pristine silver-doped carbon aerogel (A-Ag-15). However, in order to further increase the adsorption capacity, Ag-Aerogels were post-treated at various drying and curing conditions. It was found that carbonisation (pyrolysis) and activation (high-temperature oxidation) post-treatment increased the bromide removal capacity from 3.01 to 5.78 μmol/g. By comparing the point of zero charge pH (pH_{PZC}) values before and after both of the post-treatment methods, it was then hypothesised that the increase in the basicity of the Ag-Aerogel surface can be the main factor causing 92% increase in bromide removal capacity.

This study also examined the efficiency of bromide removal in the presence of NOM and chloride in two surface water samples. They reported that the Ag-Aerogels can still remove bromide, but to a lower extent, in the presence of NOM and competing anions. The decrease in bromide removal capacity was correlated to blocking of pores by negatively charged NOM molecules that could compete for available silver sites.

A further 35% decrease in bromide removal capacity was also reported where chloride was at higher concentrations than bromide in water samples. They concluded that the reduced bromide removal capacity can be a result of NOM molecules blocking the aerogel pores, as well as the presence of competing anions for silver sites on Ag-Aerogels. However, they did not distinguish the impact of chloride from the impact of NOM since the selected natural water had both constituents, and thus the individual contributions of NOM and chloride to the reduction in bromide removal capacities was unclear (Sánchez-Polo et al. 2006, 2007).

Table 2-2: Physiochemical characteristics and bromide removal capacities of Ag-aerogels (Sánchez-Polo et al., 2006, 2007)

Ag-Aerogel types	$[Ag]_0$ in Ag-Aerogel (µmol/g)	Br^- removal capacity (µmol/g)	Initial pH	pH_{PZC}	Post-treatment method	Adsorption study method	Water type
A-A	1020	4.68	6.5 - 7	9.5	Carbonisation	Dynamic/Column	Lake Zürich (Switzerland)
A-C	927	5.78	6.5 - 7	6.8	Carbonisation /Activation	Dynamic/Column	Lake Zürich (Switzerland)
A-Ag-15	927	3.01	6.5 - 7	4.5	Pristine	Dynamic/Column	Lake Zürich (Switzerland)
A-Ag-15	927	3.01	6.5 - 7	4.5	Pristine	Static/Batch	Synthetic water
A-Ag-15	927	1.91	6.5 - 7	4.5	Pristine	Static/Batch	Synthetic water
A-Ag-15	927	2.44	6.5 - 7	4.5	Pristine	Static/Batch	Lake Zürich (Switzerland)
A-Ag-15	927	2.04	6.5 - 7	4.5	Pristine	Static/Batch	Lake Greinfensee (Switzerland)
A-Ag-50	556	1.58	6.5 - 7	4.3	Pristine	Static/Batch	Synthetic water
A-Ag-200	371	0.83	6.5 - 7	4.2	Pristine	Static/Batch	Synthetic water

Von Gunten and colleagues also examined the regeneration of exhausted Ag-Aerogels using ammonia solution (Sánchez-Polo et al. 2006). According to Equation 2.1, the excess ammonia can regenerate the immobilised silver-halide precipitates to form silver–ammonia complexes so that the adsorption sites are converted from Ag^+ to $Ag(NH_3)^+$ (Sánchez-Polo et al. 2006).

$$AgX + 2NH_3 \rightleftharpoons Ag(NH_3)_2 + X^- \qquad (X^-: \text{halide}) \qquad (2.1)$$

After three consecutive adsorption/regeneration cycles, a relatively high removal efficiency of bromide from synthetic water (60 – 71%) and also a moderate bromide removal efficiency from natural surface water (31 – 56%) were achieved. In addition, the adsorption/regeneration experiments showed that there was no leaching of the organic polymer precursors in the aerogel and the concentration of the silver adsorption sites was not significantly reduced after two adsorption/regeneration cycles. However, one of the drawbacks of the Ag-Aerogels is the low ratio of bromide removal capacity and the fraction of incorporated silver within the aerogel. Therefore, this aspect needs to be improved and further research is required to synthesise materials with a higher Ag fraction. These studies suggested the need for further research and development to lower the cost of Ag-Aerogel production so that it can be integrated into large-scale treatment processes (Sánchez-Polo et al. 2006, 2007).

2.2.2 Silver-Loaded Porous Carbon Spheres (SLPCS)

In a recent study conducted by Gong et al., silver-loaded porous carbon spheres (SLPCS) were fabricated and evaluated for their bromide removal capacity for a range of synthetic water samples (Gong et al. 2013). The authors assumed that the key factor affecting the performance of silver loaded adsorbents was the nature of the support. Therefore, they decided on in-house preparation of SLPCS precursors by carbonization of poly (vinylidene chloride) porous carbon spheres that were synthesised by suspension polymerization (Qian et al. 2008). Poly (vinylidene chloride) porous carbon spheres were previously shown to have a promising iodide removal capacity from organic solutions (acetic acid) (Qian et al. 2008). In the next step, the silver impregnation was conducted using silver nitrate as the silver precursor by the incipient- wetness impregnation method (Delannoy et al. 2006). After characterisation, the resultant SLPCS were reported to have a uniform size distribution

(30–60 mesh), specific surface area (S_{BET}) of 921.3 m^2/g, 46.4 µmol/g (0.5 wt%) silver metal (Ag^0) content and pH_{PZC} equal to 9.4. No corresponding data was reported for the carbon sphere precursors before the silver impregnation.

A bromide removal capacity of 15 µmol/g (94%) was reported for 160 mg/L of SLPCS agitated in a purified water solution containing 200 µg/L of Br^- at pH 7 for 20 hours (Gong et al. 2013). The high bromide removal capacity of SLPCS was then attributed to the unique structure of the carbon sphere precursors, as well as the presence of highly active silver atoms on silver metal (Ag^0) formed inside the porous carbon spheres. They categorised the bromide adsorption data taking place in three consecutive stages based on an intraparticle mass transfer diffusion model, previously proposed by Weber and Morris (Weber et al. 1963). In the first step, a fast bromide removal was interpreted by an external mass transfer mechanism. In the second stage, which was also called the rate-limiting stage, the bromide uptake was found to be not very fast but more steady which suggested that an intraparticle diffusion mechanism was predominant. Ultimately, when the bromide residual concentration was low, the adsorption became negligible and equilibrium was reached.

The impact of solution pH, ranging from 3 to 8, as an important determinant in SLPCS bromide removal capacity was also evaluated in this study. It was found that a very weak acidic environment (e.g. pH 5) resulted in the highest (98%) bromide removal. However, an artefact was identified during the preparation of bromide solutions at very low pH (pH 3). Since hydrochloric acid was used to adjust the pH to the low pH ranges, Cl^- would potentially become a competitive anion, causing interferences in bromide removal. Table 2-3 shows a summary of bromide removal results achieved by SLPCS in the presence of several competing anions (Cl^-, NO_3^-, SO_4^{2-}, I^- and humic acid) at three different pH (5, 7 and 9). Generally, as the pH of the solution increased from 5 to 9, the adsorption of bromide decreased. This reduction in efficiency was attributed to the small positive charges on the SLPCS surface because the pH_{PZC} (9.4) was very close to the solution pH (pH 9).

Additionally, the presence of iodide had the greatest effect of all of the anions on bromide adsorption. Humic acid (HA) was also observed to significantly reduce the bromide removal efficiency to 21% when the concentration of HA was 4 mg/L at

neutral pH. The impacts of the competitive inorganic species observed at concentrations below 10 mg/L were then ordered as follows: $I^- > SO_4^{2-} > NO_3^- > Cl^-$. The competitive inorganic anions were proposed to occupy the adsorption sites and thus deteriorate the bromide removal. Furthermore, the high impact of iodide on bromide removal was interpreted according to the higher stability (lower solubility) of silver iodide ($K_{sp} = 8.5 \times 10^{-17}$) compared to that of silver bromide ($K_{sp} = 5.4 \times 10^{-13}$). Two interfering mechanisms were reported with regards to negatively charged HA organic compounds: (i) occupying the bromide adsorption sites in SLPCS and (ii) blockage of the pathways for bromide to access the carbon pores due to the large molecular size of the HA molecules. Although this study showed the advantages of SLPCS for bromide removal, mechanisms for the interactions between bromide and SLPCS were neglected. No pathways for the immobilisation of Ag^0 nanoparticles to Ag^+ and the consequent silver-bromide formation were reported (Gong et al. 2013).

Table 2-3: Comparison of competitive adsorption on SLPCS between bromide and other coexisting anions at various initial solution pH (Gong et al., 2013)

Solution condition	**Bromide removal (%)**		
	pH 5	**pH 7**	**pH 9**
Deionized water	98	90	78
$[Cl^-]_0$ = 20 mg/L	77	83	75
$[NO_3^-]_0$ = 5 mg/L	92	83	93
$[SO_4^{2-}]_0$ = 40 mg/L	28	30	28
$[I^-]_0$ = 2 mg/L	80	9	1
$[HA]_0$ = 4 mg/L	–	21	–

2.2.3 Silver-Doped Polymeric Cloth (Ag-cloth)

A novel adsorbent called silver-doped polymeric cloth (Ag-cloth) was studied for its potential in the removal of bromide and iodide from waters (Polo et al. 2016). The Ag-cloth substrate was prepared by transferring a methacrylic-based polymer into the cloth material using an electrospinning methodology. After cloth generation, silver nanoparticles were included by specific interactions between the polymer chemical groups and Ag atoms. To reduce the generated Ag^+ to Ag^0 on the cloth surface, a UV radiation method was used. The resultant Ag-cloth was reported to have a very low specific surface area (S_{BET} = 5 m^2/g) and no porosity. To determine the bromide

removal capacity of the Ag-cloth, the Ag-cloth was reported to require an activation by oxidation with excess hydrogen peroxide (H_2O_2) so that the immobilisation of Ag^+ on Ag-cloth surface is ensured. The main objective of the immobilisation was to guarantee selective adsorption of the bromide so that the resultant silver bromide precipitates are retained on the cloth and are not passed into the solution (Polo et al. 2016).

Table 2.4 indicates the influence of H_2O_2 concentration and water matrix chemical composition on bromide removal capacity, where $[Br^-]_0$ = 25 µM. According to these results, the removal capacity of the Ag-cloth was approximately doubled by increasing the initial H_2O_2 concentration from 25 to 65 µM. This behaviour was explained by Ag^+ being produced when Ag^0 reacts with H_2O_2, so that a higher oxidant concentration results in a higher concentration of Ag^+ attached to the Ag-cloth surface. However, as initial H_2O_2 concentration was further increased to 75 µM, a slight decrease in bromide removal capacity was reported. The latter behaviour was correlated to the Ag^+ reduction to Ag^0 by action of the superoxide radical at a very high oxidant concentration (Henglein et al. 1981; He et al. 2011; Jones et al. 2011).

Table 2-4: Bromide removal capacities of the Ag-cloth as a function of the type of water, initial H_2O_2 concentration and water matrix compositions (Polo et al. 2016)

Type of water	**Initial pH**	**$[H_2O_2]_0$ (µM)**	**Br^- capacity µmol/g**	**$[Cl^-]_0$ (µM)**	**$[Br]_0$ (µM)**	**$[TOC]_0$ (mgC/L)**
Ultrapure	6.5 ± 0.5	25	8.14	---	25	---
Ultrapure	6.5 ± 0.5	35	9.39	---	25	---
Ultrapure	6.5 ± 0.5	45	12.39	---	25	---
Ultrapure	6.5 ± 0.5	55	15.52	---	25	---
Ultrapure	6.5 ± 0.5	65	16.27	---	25	---
Ultrapure	6.5 ± 0.5	75	15.64	---	25	---
Simulated water	7.0	75	11.01	846.3	25	5
Wastewater	7.8	75	10.39	987.3	25	12
Wastewater	7.8	95	17.15	987.3	25	12
Wastewater	7.8	105	16.90	987.3	25	12
Wastewater	7.8	304	18.27	987.3	25	12

The applicability of Ag-cloth for bromide removal was also studied in a simulated water and a real wastewater sample. At the highest oxidant concentration ($[H_2O_2]_0$ = 75 µM), a significant decrease in bromide removal capacity of the Ag-cloth was observed for both simulated water and wastewater. For 75 µM H_2O_2, 30 and 34% deterioration in bromide removal capacity of the Ag-cloth was reported in the treatment of the simulated water and wastewater, respectively. This comparison was made to illustrate that the presence of differing anions and organic matter can reduce the capacity of Br^- removal. A relatively high adsorption capacity of tannic acid (TA) molecules on the Ag-cloth equal to 156 mg/g Ag-cloth, was also reported, which presumably means this adsorbent material is susceptible to interference by organic matter present in water samples (Polo et al. 2016). Although Ag-cloth was shown to be attractive due to its selectivity for bromide and its potential for low silver loss, its large-scale production seems not to be economical in cases where the primary objective is bromide reduction.

2.2.4 Silver-impregnated Activated Carbon (SIAC)

Silver-impregnated activated carbon (SIAC) is known as an excellent point-of-entry/point-of-use (POE/POU) water disinfectant (Bell Jr 1991). The incorporation of silver inhibits the bacterial growth in the activated carbon so that the lifetime of SIAC is increased. In addition to this advantage, a possible application of SIAC in water treatment is the removal of halides from drinking water sources, with the ultimate aim of disinfection by-product minimisation (Hoskins et al. 2002; Watson et al. 2016; Chen et al. 2017). To date, two laboratory studies examining SIAC treatment for bromide removal and the formation potential of selected DBPs have been published (Watson et al. 2016; Chen et al. 2017).

Watson et al. (2016) investigated the efficiency of a commercial SIAC (Norit 18×40 AG1, 0.1% Ag) for the removal of bromide and NOM from a matrix of synthetic waters with variable NOM, halide, and alkalinity concentrations, followed by an investigation into the formation potential of selected DBPs (Watson et al. 2016). However, an enhanced coagulation (EC) treatment with alum ($Al_2 (SO_4)_3.18H_2O$) was employed prior to SIAC treatment (Figure 2.1(a)). More than 90% of bromide was removed by the SIAC treatment only. The combination of EC with SIAC treatment removed more than 90 and 70% of bromide and dissolved organic carbon

(DOC) from the synthetic water sample, respectively. The maximum bromide removal capacity was equated to 1.4 µmol/g across all SIAC treated samples. The bromide removal mechanism was reported to be similar to that described for iodide by Hoskins and colleagues (Hoskins et al. 2002). In other words, the bromide removal was attributed to the deposition of insoluble silver bromide precipitates on the SIAC due to its low solubility product ($K_{sp} = 5.4 \times 10^{-13}$).

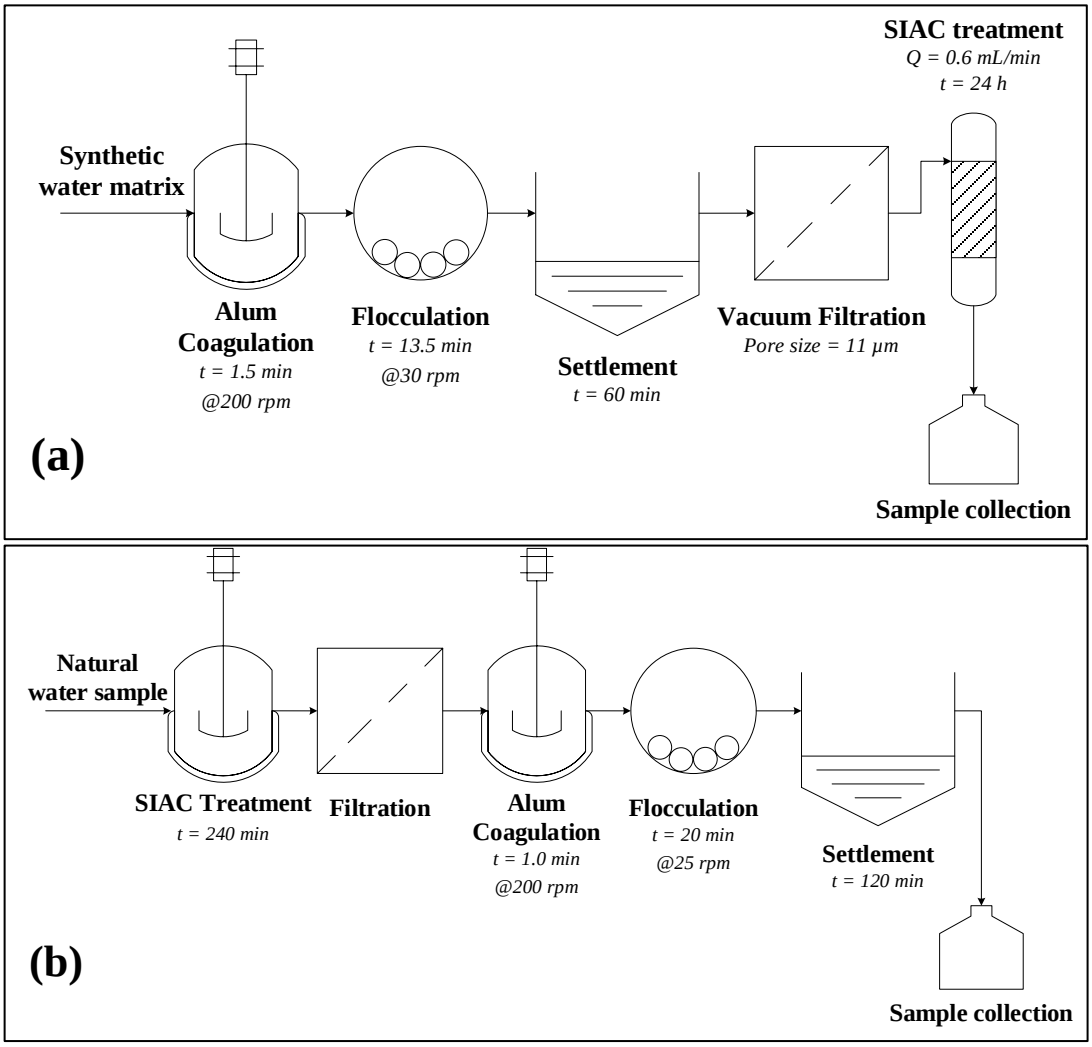


Figure 2-1: A comparison between the bromide removal conditions used in two different SIAC studies (a) (Watson et al. 2016) and (b) (Chen et al. 2017).

Additionally, by comparing the bromide removal results obtained from a granular activated carbon (GAC) which was equivalent to the SIAC in all aspects apart from the silver content, physical adsorption of bromide onto the activated carbon precursor itself was also considered for the further removal of bromide by SIAC. The DOC adsorption onto SIAC was largely correlated to the hydrophobic and electrostatic

interactions. Although a further 21 ± 5% increase in DOC removal was observed after the SIAC treatment, the influence of a small amount of silver sites on SIAC (1 mg silver per gram of SIAC) was reported to be negligible. It was proposed that the DOC removal is primarily controlled by adsorption onto the activated carbon, by hydrophobic interactions. The coexistence of chloride in the synthetic water matrix at environmentally representative concentrations (Br^-/Cl^- ratio of 1:300 by weight) was further investigated to simulate a more complex environment. Although chloride was presented in much higher concentrations than bromide, SIAC still performed efficiently in removing bromide in all samples (No reported data). Due to the lower solubility of AgBr compared to that of silver chloride (AgCl, $K_{sp} = 1.8 \times 10^{-10}$) anion exchange of chloride for bromide was proposed to have taken place in silver chloride precipitates on the surface of the SIAC (Watson et al. 2016).

A similar interpretation was used to describe the adsorption of iodide on to AgCl-filled activated carbon (Ho et al. 1981; Karanfil et al. 2005). The latter studies indicated that SIAC materials are promising for the removal and sequestration of iodide (^{129}I) from water through the formation of a silver iodide (AgI, $K_{sp} = 8.5 \times 10^{-17}$) surface precipitate and also the conversion of AgCl to AgI through chloride-iodide exchange reactions. The specific ultraviolet absorbance at 254 nm ($SUVA_{254}$), as an indicator of the aromatic content of NOM was also measured before and after EC treatment and after the combined treatment (EC/SIAC) (Watson et al. 2016). EC treatment was found to reduce the initial $SUVA_{254}$ by 67 ± 20%, whereas the initial $SUVA_{254}$ was reduced by 89 ± 11% for the combined EC/SIAC treatment. The major conclusion obtained from the $SUVA_{254}$ study was that the DOC remaining after the combined treatments had low $SUVA_{254}$ and therefore potentially had a lower reactivity and formation potential for selected DBPs (Watson et al. 2016).

In another study conducted by Chen et al. 2017, several combinations of carbon pre-treatment (i.e. pre-oxidation) and silver impregnation pathways were employed for the preparation of SIAC and to find out an optimum silver impregnation protocol (Chen et al. 2017). The main objective of pre-oxidation of the carbon was for the initiation of negatively charged oxygen containing groups (e.g. carboxylic acids) in order to achieve further attachment of Ag^+ during the silver impregnation step. Four of the in-house impregnated SIAC samples were selected to identify the effect of the initial

characteristics of the carbon precursor on Br^- removal (Table 2.5). Comparing the specific surface area (S_{BET}) values of the carbons before and after silver impregnation showed a decrease in S_{BET} values after silver impregnation. This observation was attributed to one or a combination of following reasons: (i) pore blockage by oxygen surface groups produced by severe pre-oxidation using concentrated nitric acid (15.7 N HNO_3); (ii) electrostatic repulsion of surface probe molecules (nitrogen); (iii) wall erosion and collapse and destruction of carbon micro pore walls by concentrated nitric acid (Chen et al. 2017).

The bromide uptake experiments were carried out in purified water containing 306.6 µg/L Br^- and 25 mg/L SIAC (Chen et al. 2017). Up to 95% percent bromide removal was observed. Interestingly, they found that the S_{BET} values of the SIAC were directly proportional to bromide removal efficiency in purified water. According to the amount of SIAC added (25 mg/L), the minimum silver concentration required for the precipitation of 306.6 µg/L initial Br^- in purified water is only about 150 µmol/g and the silver content of all SIAC were well above this theoretical value. Therefore, no correlation was reported between SIAC silver content and Br^- uptake in purified water and the higher silver content did not result in a better Br^- removal. The enhanced bromide removal capacities correlating with the higher S_{BET} values were attributed to the presence of more active adsorption sites and ease of access by free Br^- to precipitate with the corresponding Ag^+ on the SIAC surface (Chen et al. 2017). Therefore, it was deduced by the authors that maintaining a high S_{BET} during SIAC preparation, including pre-oxidation of carbon precursors and silver impregnation, was the main factor controlling the capacity for bromide removal (Chen et al. 2017).

To evaluate the impact of background water matrix on the bromide removal capacity, a natural water sample was treated using a commercially available SIAC (Nucon Nusorb A 20×40, 4.03% Ag), with no further modification (Chen et al. 2017). It was shown that by increasing the chloride concentration added into the natural water sample from 10 to 200 mg/L, the bromide removal efficiency consequently decreased from approximately 70% to 84%. The main explanation for these results was related to the chloride competition (Br^-/Cl^- ratio of 1:33 to 1:670 by weight) for silver sites on SIAC. Along with the addition of 2.5 mgC/L of NOM isolate to this natural water sample, a further 15% decrease in bromide removal was observed. In this regard, two

possible mechanisms were suggested for the NOM matrix interference. First, the more reactive NOM constituents can compete with bromide to reach and deactivate the adsorption sites on the SIAC surface (site competition). Additionally, the larger NOM molecules could block the SIAC smaller pores and prevent the Br^- from reaching available adsorption sites into these pores (pore blockage). Both pathways could result in a decreased bromide removal efficiency (Chen et al. 2017).

Similar to the study of Watson et al. (2016), the impact of coagulation/flocculation combined with a SIAC treatment to increase the overall bromide removal efficiency was evaluated. For this purpose, an EC with alum ($KAl(SO_4)_2 \cdot 12H_2O$) process was employed after the SIAC treatment. A schematic illustration of this study is shown in Figure 2.2(b). The addition of alum after SIAC treatment was found to be inefficient for the removal of more bromide from the natural water sample. Up to 40% Br^- removal was achieved during the SIAC treatment, while the addition of alum did not make a considerable difference. Following the addition of alum to the natural water sample containing SIAC, a 45% decrease in DOC concentration was observed, where the 5.4 mgC/L initial DOC was reduced to about 3 mgC/L. It was also reported that the floc formation during the coagulation did not deteriorate the Br^- uptake by SIAC. It was previously reported by this research group that natural waters with $SUVA_{254}$ > 2.0 L/mg-M are relatively high in electron-rich aromatic carbon groups and consequently high in DBP formation potential. However, no results were found with respect to $SUVA_{254}$ value after the SIAC/EC treatment.

Table 2-5: Physiochemical characteristics of various SIAC used for bromide removal application (Chen et al. 2017)

SIAC names	Before silver impregnation			After silver impregnation			Pre-treatment	Impregnation
	S_{BET}*	Oxygen (%)	pH_{PZC}	S_{BET}*	Oxygen (%)	$[Ag]_0$ in SIAC (µmol/g)		
20B-05	1748	0.9	5.4	1681	19.6	333.7	Pre-oxidized with 15.7 N HNO_3 at 160°C	0.5 M $AgNO_3$ at 160°C
F400-05	978	2.4	9.2	904.8	15	213.2	Pre-oxidized with 15.7 N HNO_3 at 90°C	0.5 M $AgNO_3$ at 90°C
WC800-5	713	4.1	10.4	539.1	14.6	1001.2	Pre-oxidized with 15.7 N HNO_3 at 90°C	0.5 M $AgNO_3$ at 90°C
HD300-05	642	4.1	6.9	370.8	18.9	778.7	Pre-oxidized with 15.7 N HNO_3 at 90°C	0.5 M $AgNO_3$ at 90°C

* ***S_{BET}*** *= specific surface area which was calculated by the authors using the Brunauer-Emmett-Teller (BET) model*

Table 2-6: A comparison between the physiochemical characteristics and bromide removal capacities of two commercially available SIAC used in (Chen et al. 2017)[1] and (Watson et al. 2016)[2] studies

SIAC names	$[Ag]_0$ in SIAC (µmol/g)	Br^- capacity (µmol/g)	DOC removal (%)	SIAC Efficiency (%)
[1] Nucon (Nusorb A 20×40)	370.8	37.5	45	10.1
[2] Norit (18×40 AG1)	9.3	1.4	77	15.5

2.3 Scope of Project

The majority of published studies on silver-incorporated adsorbents for the removal of halide from water have neglected the quantification of silver leaching while the extent of bromide removal is measured. Although a few studies monitored the dissolved silver in the water samples, free Ag^+ and the total amount of silver leaching (Ag_{Total}) were not distinguished. Ag_{Total} is defined as follows:

$$Ag_{Total} = Ag^+ (aq) + AgX (aq) + Ag–NOM (aq) \quad (2.5)$$

where the Ag^+ (aq), AgX (aq) and Ag–NOM represent the concentration of free Ag+ in solution, the concentration of silver in silver-halide precipitates in solution and silver–NOM complexes formed in solution, respectively (i.e. all silver in solution and excluding silver on the surface of SIAC).

Several studies have demonstrated that precursors to the formation of carcinogenic halogenated DBPs are most likely sourced from two water constituents: a) naturally occurring bromide ion and b) natural organic matter. Although SIAC has been shown to be a promising material for the minimisation of bromide concentration in treated water (Watson et al. 2016; Chen et al. 2017). However, due to the high affinity of organic molecules towards silver, it has been commonly reported that the SIAC capacity for halide removal would be significantly decreased in the presence of organic molecules (Sánchez-Polo et al. 2006, 2007; Watson et al. 2016; Chen et al. 2017; Gong et al. 2013). This reduction was attributed to blockage of adsorbent pores through the bigger NOM molecules (physisorption), as well as direct complexation reactions of negatively charged NOM molecules with available Ag^+ sites (Sánchez-Polo et al. 2006, 2007; Watson et al. 2016; Chen et al. 2017; Gong et al. 2013). However, the current understanding about the impact of physicochemical characteristics of NOM on silver-incorporated adsorbent is weak. Therefore, the interpretation of the effect of NOM on the bromide removal capacity of silver-incorporated materials is not clear.

In this study the extent of silver leaching from a range of commercially available SIAC materials was determined through the parallel measurements silver leached out in various dissolved and precipitate forms. One of the main objectives of this research

was to better understand the mechanisms of silver leaching from SIAC under typical water treatment conditions in order to develop approaches to minimise silver leaching during bromide removal applications. Additionally, this study was planned to further explore the impact of variations in chemical compositions and molecular weight distribution of the NOM isolates on the kinetics and capacity of bromide adsorption and the extent of silver leaching from the adsorbent into the treated water.

Chapter 3

Interferences in Bromide Removal and Silver Leaching Properties of Silver-impregnated Activated Carbon

3.1 Abstract

In this chapter, three types of commercially available silver-impregnated activated carbon (SIAC) and one type of granular activated carbon (GAC) without silver impregnation were tested for their capacity to remove bromide from samples of both synthetic and real water. Comparison of the bromide removal capacities of the different types of SIAC and the GAC confirmed that the incorporation of silver into the activated carbon matrix is highly efficient in removing bromide, although substantial variation was observed between the different materials tested. The Norit SIAC, which removed up to 95% of initial bromide (12.5 µM), was studied in more detail for its capacity to adsorb bromide during three consecutive adsorption tests. Additionally, several other factors determining the practicality of the use of this SIAC for selective removal of bromide such as the extent of silver leaching and the natural organic matter (NOM) removal capacity were also investigated in this study. Although, up to 95% (12.2 µmol/g) of the initial bromide was removed during the first batch, the bromide removal capacity decreased by 40% during the second and third tests. This reduction in bromide removal capacity was attributed to the decrease in Ag^+ incorporated into Norit SIAC. The kinetics studies revealed that more than 66% of the bromide was removed in 30 minutes ($[Br^-]_{t=30min}$ = 4.2 µmol/g) and that the removal was in accordance with first order kinetics. However, after 30 to 120 min, the agreement between the first order kinetics model and the experimental data became less consistent, This may be attributed to the reduction of available adsorption sites, potentially caused by silver leaching. To assess the impact of dissolved organic carbon (DOC) on the bromide removal capacity of Norit SIAC, 3.6 mgC/L of tannic and gallic acid as well as 1 to 4 mgC/L of Suwannee River Humic (SRHA) and Fulvic (SRFA) acids were added. Results showed that the rate of bromide removal in a solution free of organics was faster within the first 30 minutes in comparison to those in the presence of dissolved organics. It was also observed that the presence of dissolved organics with various functionalities would alter the extent of silver leaching and bromide removal properties using SIAC. However, the physical adsorption (physisorption) of bromide to the SIAC resulted an overall bromide removal capacity remaining unchanged after a longer contact time (180 minutes).

3.2 Introduction

Elevated concentrations of naturally occurring bromide (Br^-) in drinking water sources cause various water quality problems, upon final disinfection (Richardson et al. 2007). The presence of bromide was found to expedite the formation and speciation of various classes of organic and inorganic disinfection by-products (DBPs), given that brominated DBPs (Br-DBPs) have been found to be more toxic and carcinogenic than their chlorinated analogues (DBPs) (Pan et al. 2013; Sharma et al. 2014; Y. Yang et al. 2014; Criquet et al. 2015). Therefore, treatment and distribution of drinking water containing these high bromide concentrations creates numerous difficulties for water utilities. A recent study reported that many drinking water sources in Western Australia, mostly near the coastal regions, contain elevated concentrations of bromide by worldwide standards (ranging from 0.4 to 8.4 mg/L) (Gruchlik et al. 2015). However, there is currently no economically viable method of the selective removal of bromide in drinking water treatment processes (Watson et al. 2012). While membrane and electrochemical desalination methods are effective in the removal of bromide, these are often not considered economical in cases where the primary objective is bromide reduction.

Silver-impregnated adsorbents are promising technologies for adsorption of halides from water (Ho et al. 1981; Hoskins et al. 2002) and these have the potential for development for selective removal of bromide in municipal drinking water treatment. The use of silver-filled composites in sustainable point-of-use drinking water treatment processes has become ubiquitous, especially for the purpose of disinfection (Oyanedel-Craver et al. 2008; van Halem et al. 2009; Dankovich et al. 2011; Ren et al. 2013). As discussed in Chapter 2, silver-doped carbon aerogels (Ag-aerogels) and silver impregnated activated carbon (SIAC) are attractive options due to their selectivity for bromide (Sánchez-Polo et al. 2007; Gong et al. 2013; Watson et al. 2016; Chen et al. 2017). Although efforts have been made to understand the bromide removal mechanisms, little is known concerning the silver leaching behaviour of silver-impregnated materials. In general, issues related to the dissolution and the leaching of silver into the treated water have limited their application in large-scale water treatment applications (Kumar et al. 2005; Benn et al. 2008; Liu and Hurt 2010; Zhang et al. 2012; Dobias et al. 2013). Although the mechanism of silver leaching is not well-understood, two silver leaching mechanisms were proposed in presence of

oxidant (e.g. dissolved oxygen and hydrogen peroxide): (i) physical loss of silver metal (Ag^0) caused by the experimental artefact and (ii) desorption and release of chemisorbed silver ions (Ag^+) from the surface of silver-containing materials into solution (Dobias et al. 2013).

In this study, the potential of three types of commercially available SIAC and one type of GAC, without silver impregnation, to reliably remove bromide were investigated. Norit SIAC was then considered for further evaluation of its Br^- removal and silver leaching properties in presence and in the absence of two natural organic matter (NOM) isolates. In addition, due to the complexity of NOM mixtures, tannic acid (TA) and gallic acid (GA) (Figure 3-1) were chosen as NOM surrogates to systematically examine their affinity to Norit SIAC during the bromide adsorption. Finally, a raw water sample collected from a drinking water source in Western Australia was used to assess the bromide removal capacity of SIAC

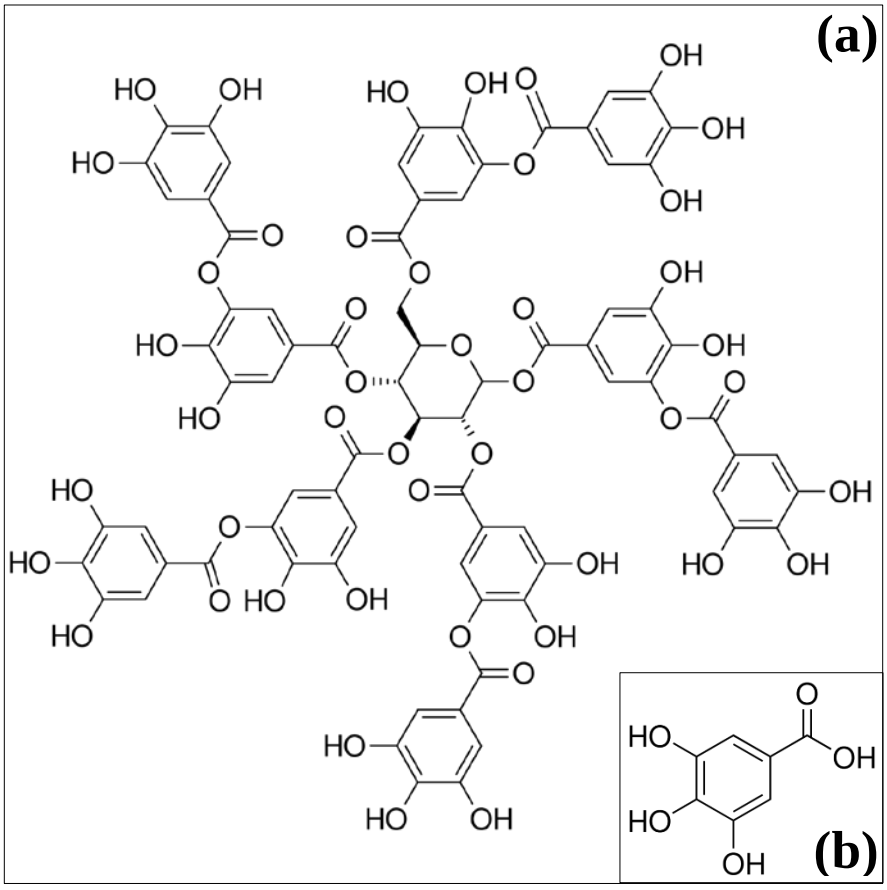


Figure 3-1: Molecular structures of (a) Tannic acid and (b) and Gallic acid (inset)

3.3 Materials and Methods

3.3.1 Chemicals, Reagents and Analytical Methods

Norit AG grade silver-impregnated granular activated carbon with mesh size of 18×40 (0.42–1.00 mm) provided by Cabot Norit®, Amersfoort, The Netherlands, silver-impregnated activated carbon with mesh size of 12×30 (1.70–0.60 mm) purchased from HayCarb Holdings, Australia and SilverSol™ Coated WT400 granular activated carbon with mesh size of 20×40 (0.42–0.84 mm) purchased from Nano Silver Manufacturing SDN BHD (NSM™) and minimal silver content of 0.1, 0.05 and 0.04 (wt%) were used throughout this study. FILTRASORB® 400 granular activated carbon (F400-GAC) with an effective size of 0.55–0.75 mm with no silver content was provided by Calgon Carbon Corporation, Pittsburgh, PA.

Sodium bromide (NaBr ReagentPlus®, ≥99%), potassium nitrate (KNO_3 ACS reagent, ≥99.0%), were purchased from Sigma-Aldrich. All other reagents used, including sodium chloride (NaCl), sodium hydroxide (NaOH), nitric acid (HNO_3, 70%) and hydrochloric acid (HCl, 34%) were supplied by Ajax Finechem Pty Ltd. Silver nitrate ($AgNO_3$ AR grade, ≥99.5%) was obtained from Rowe Scientific Pty Ltd. Tannic acid ($C_{76}H_{52}O_{46}$) and Gallic acid ($C_7H_6O_5$) from Sigma were of ACS reagent grade purity and were used without further purification. Suwannee River Humic Acid (SRHA, 2S101H) Suwannee River Fulvic Acid (SRFA, 2S101F) were purchased from the International Humic Substances Society (IHSS, St. Paul, MN). Ultrapure water produced by an ELGA water purification system (resistivity of 18.2 MΩ.cm) was used throughout this study for the preparation of reagents and solutions unless otherwise indicated.

Bromide concentrations were measured using a Dionex ICS 3000 ion chromatography system with a Dionex IonPac AS9-SC (4.0 mm × 250 mm) analytical column, where the detection limit was 5 µg/L.

The dissolved organic carbon (DOC) concentration was measured using a total organic carbon (TOC) analyser connected to an auto-sampler (TOC-LCSH/CSN Model, Shimadzu Co., Kyoto, Japan). Calibration of the TOC instrument was carried out using

potassium hydrogen phthalate standards (1–5 mg/L). The correlation coefficients of the calibrations were >0.99 at all times.

The ultraviolet absorbance at 254 nm (UV_{254}) of all samples was measured using a Cary 60 UV–Vis Spectrophotometer (Agilent Technologies, Australia) with a 1 cm quartz cell. The specific UV absorbance ($SUVA_{254}$) was determined by dividing the absorbance at 254 nm by the DOC value.

The total silver concentrations in solutions were measured using a Varian Model SpectrAA 50 flame atomic absorption spectrophotometer (AAS) with a nominal limit of detection (LOD) of 0.02 mg/L of Ag. A real water matrix from a groundwater bore in Western Australia with specifications given in Table 3.1 was used in this study.

In order to evaluate the dissolved and precipitated silver concentration in the solutions, the SIAC was first removed from the solution by filtering the solution (500 mL) through a qualitative filter paper (Whatman® grade 4, 20–25 μm nominal pore size), followed by the addition of 6 mL concentrated HNO_3. The solution was vigorously stirred and heated until the volume was reduced to about 50 mL. The final solution was made up to 100 mL with purified water in a volumetric flask prior to analysis using AAS. In order to determine the point of zero charge pH (pH_{PZC}) of SIAC, the pH was adjusted by addition of NaOH (10 mM) or HNO_3 (10 mM) to sodium nitrate ($NaNO_3$: 50 mL of a 0.01 M solution). SIAC (0.15 g) was added to each of the different pH solutions and the solutions were agitated for 72 h (Putra et al. 2009). All experimental results reported as mean ± percentage error obtained from a minimum of two repeats.

Table 3-1: Selected water quality parameters of the real water matrix

Measured parameters	**Initial values**
Chloride (mg/L)	43
Bromide (μg/L)	155
Iodide (μg/L)	5
DOC (mgC/L)	3.37
UV_{254} (cm^{-1})	0.238
pH	7.1

3.3.2 Batch Adsorption Studies

Batch adsorption tests were carried out by adding specified amounts of SIAC or GAC to various synthetic bromide solutions. Isothermal kinetic and equilibrium studies (30 ± 0.5 °C and 150 rpm) were performed by agitating water samples in flasks using Lovibond jar testing apparatus with 6 stirring places equipped with a temperature controlled water bath. Adsorption parameters were obtained using the following equations:

$$q_e = \frac{V_L}{m_A}(C_0 - C_e) \quad (3.1)$$

$$q_e = \frac{q_m b C_e}{1 + b C_e}(Langmuir) \quad (3.2)$$

$$q_e = K C_e^{\,1/n}(Freundlich) \quad (3.3)$$

where q_e is the equilibrium solid-phase concentration per unit mass of SIAC; C_0 and C_e are the initial and equilibrium bromide concentrations (µmol/L), respectively; V_L (L) is the total volume of solution and m_A (g) represents the mass of SIAC; q_m, b, K and n are constants specific to each isotherm model. In order to compare the ion uptake and leaching capacities of the SIAC for all experiments, the following correction factor was also used:

$$C_t = \frac{V_L}{m_A}(C_{t,ins}) \quad (3.4)$$

where C_t (µmol/g) is the liquid-phase concentration per unit mass of SIAC, $C_{t,ins}$ (µmol/L) is the liquid-phase concentration read by instrument. All fitting of experimental data to adsorption isotherm and kinetics models were performed using *lsqnonlin* nonlinear least-squares curve fitting function in MATLAB R2014a (MathWorks, Natick MA, USA) that uses the Levenberg–Marquardt algorithm. No buffer solution was used for the purpose of pH adjustment so that interferences by coexisting ions could be prevented. The pH values were adjusted by addition of NaOH (10 mM) or HNO_3 (10 mM) and monitored during the experiments.

3.4 Results and Discussion

3.4.1 Bromide Removal Efficacy Comparison between GAC and SIAC

According to previous studies a combined influence of silver content and point of zero charge (pH_{PZC}) on activated carbon determines the overall capacity of SIAC materials in removing bromide from water (Sánchez-Polo et al. 2006; Chen et al. 2017).

Therefore, the concentration of initial silver incorporated into SIAC as well as the pH_{PZC} values were plotted for each of the adsorbents in Figure 3.1. At pH 6.5, the SIAC or the GAC have a net positive charge ($pH_{solution}<pH_{PZC}$). Therefore, the electrostatic forces between the positively charged SIAC and bromide are attractive, which is desirable for Br^- adsorption. For the fresh GAC (pH_{PZC} = 9.7), only 25% Br^- removal was achieved because electrostatic interaction was the only mechanism for Br^- adsorption; however, the removal of bromide by used GAC was expected to be much lower. A large increase in Br^- removal (up to 97%) was observed for the all the SIAC adsorbents, explained by a surface co-precipitation between bromide ions and silver ions on the SIAC surface. As shown in Figure 3-2, the pH_{PZC} and silver content of Norit SIAC were the lowest and highest, respectively compared to other adsorbents. Due to its high silver content, which was in excess compared to the initial bromide concentration (12.5 µmol/g), a maximum capacity for bromide removal was reached.

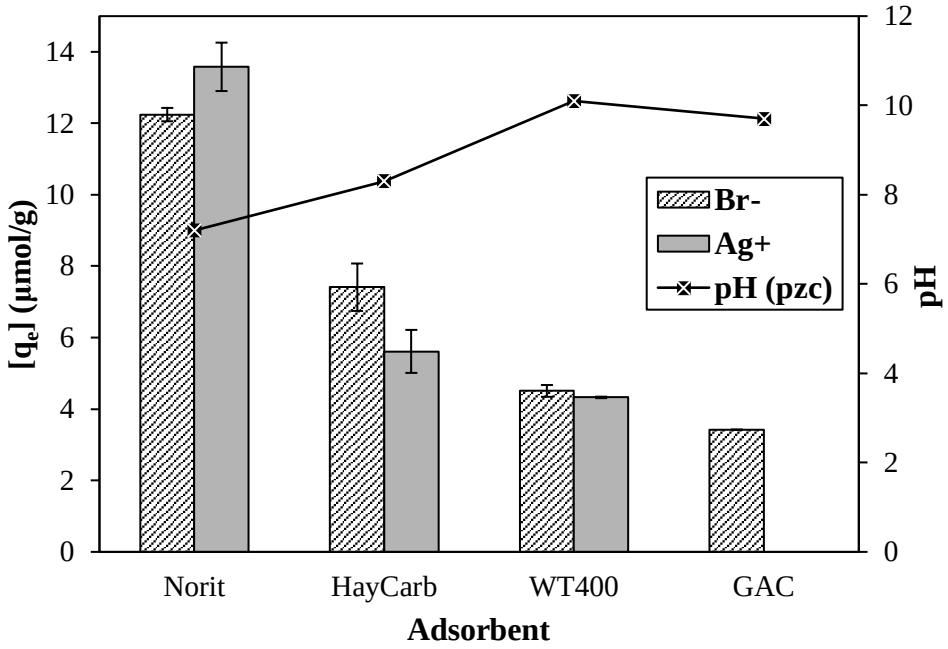


Figure 3-2: The concentration of (grey) initial silver incorporated into SIAC and (white) the concentration of bromide removed in 200 mL of solution containing 12.5 µM of Br^- and 200 mg of various SIAC and GAC adsorbents after 24 h contact time at pH_0 6.5

Accordingly, the higher capacity of HayCarb SIAC than WT400 can also be attributed to its higher silver content which was 5.6 µmol/g compared to that of WT400 (4.3 µmol/g). It is worthwhile noting that the extent of bromide removed through the HayCarb (7.1 µmol/g) was greater than the amount of silver incorporated into this type

of SIAC (5.6 µmol/g). As discussed earlier, this extra Br^- adsorption is possibly caused by the combined influence of surface co-precipitation and electrostatic forces between SIAC and bromide in the solution.

3.4.2 Silver Leaching Studies

The leaching of silver from Norit and HayCarb SIAC the two SIAC samples that had the highest bromide removal performance, was tested for six initial concentrations of bromide during 24 hours of contact (Figure 3.2). No bromide residual was detected for the experiments in the presence of Norit SIAC. Higher values for silver leaching were observed with the solutions with the lower bromide concentration, with the maximum of 7.6 and 3 µmol/g of total silver content, respectively, from the Norit and HayCarb SIAC. The greater concentration gradient between the bromide solution and the available Ag^+ in SIAC can possibly accelerate the leaching process of silver from the SIAC to the liquid-phase, causing the higher extent of silver leaching. However, the formation of AgBr precipitates would deactivate the available silver sites on SIAC so that the extent of leaching of silver ions over time is reduced. It is also hypothesised that the silver leaching from SIAC may be a mechano-chemical process. That means the silver coatings within the carbon are susceptible to possible damage and detachment from the SIAC due to high turbulence intensity and long-term operation. Therefore, the relationship between the extent of silver leaching and the kinetics of bromide removal were further studied.

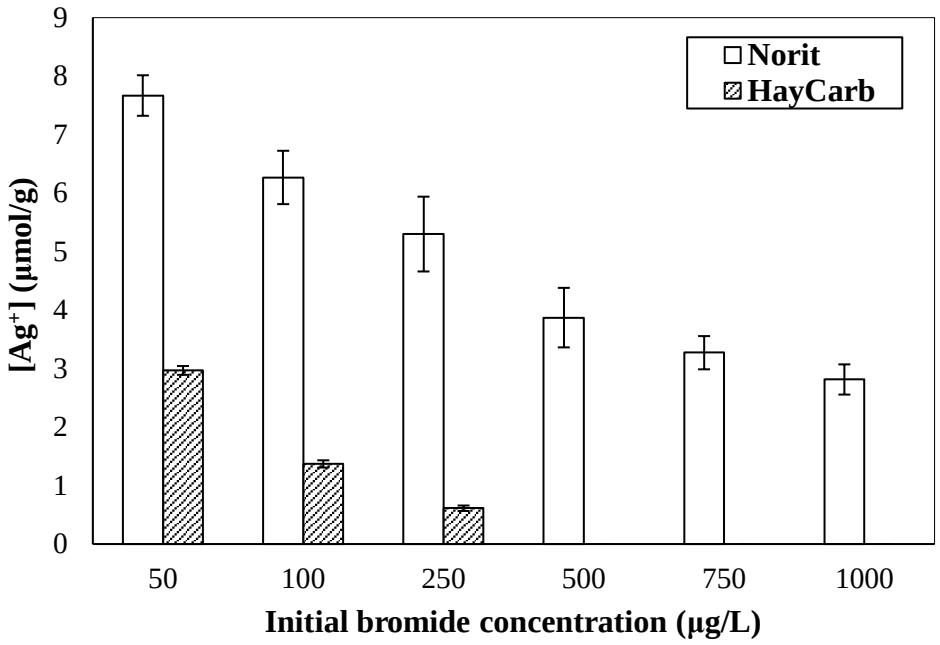
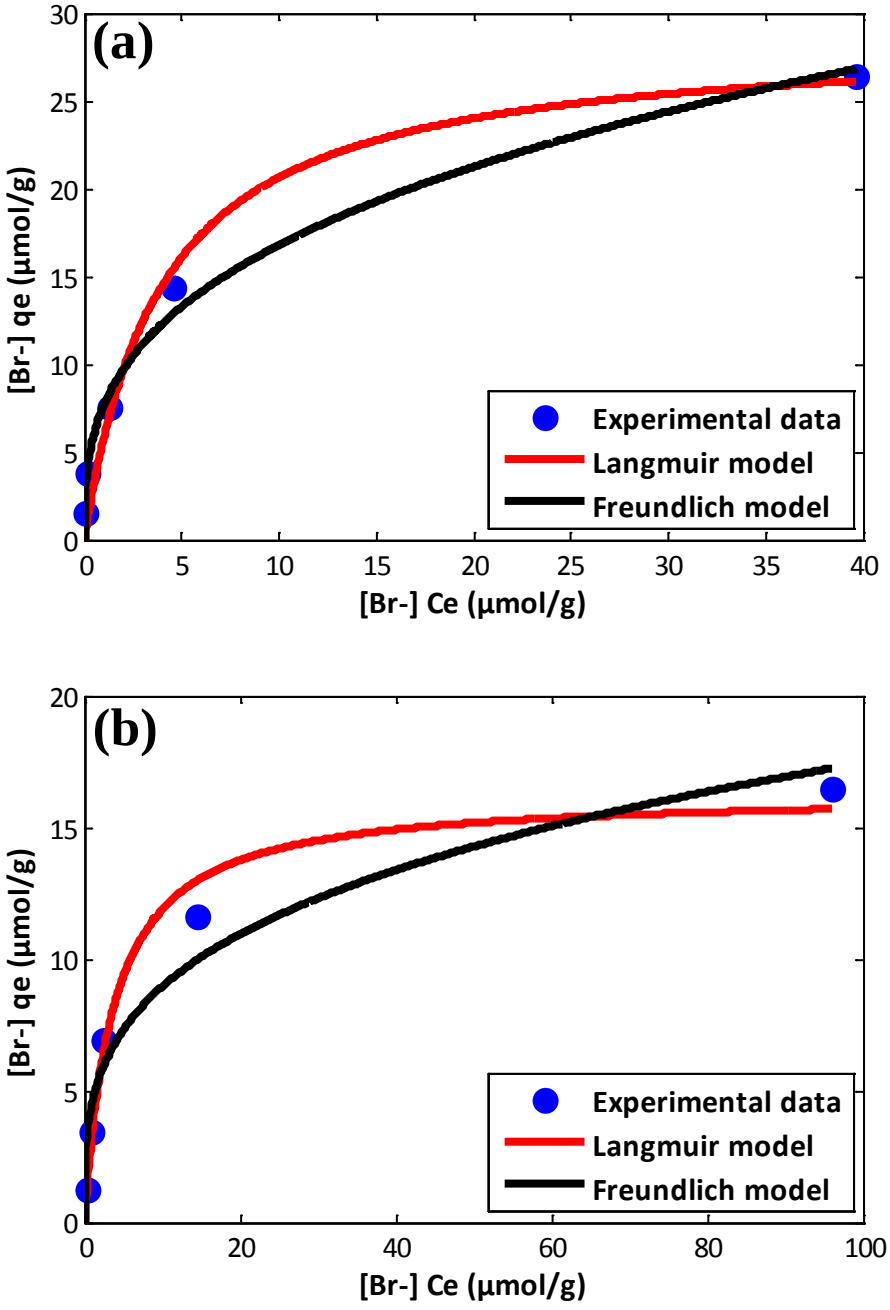


Figure 3-3: The silver residual in solution after a 24 hours batch experiment at six different initial concentration of bromide (0.625, 1.25, 3.125, 6.25, 9.375 and 12.5 µM) using 200 mg of Norit (white) and HayCarb (hashed) SIAC in 200 mL solution at pH_0 6.5

3.4.3 Dynamic Adsorption Modelling of Bromide

Three consecutive adsorption isotherm studies were conducted using two well-known isotherms, Langmuir and Freundlich. The detailed results are shown in Figure 3-4 and Table 3-2. The Langmuir isotherm assumes monolayer adsorption onto a surface containing a finite number of adsorption sites, of uniform strategies of adsorption with no transmigration of adsorbate in the plane of surface. The Freundlich isotherm model assumes heterogeneous surface energies, in which the energy term in the Langmuir equation varies as a function of the surface coverage (Beck 1973). Removal of bromide was found to be fast during the first 30 minutes after which it slowed before reaching a steady state concentration around 180 min (data not shown). Three consecutive adsorption isotherms for the Norit SIAC in contact with a range of synthetic bromide solutions (250, 500, 750, 1000 and 2000 µg/L) are shown in Figure 3-3. After each equilibrium, Norit samples were collected, dried and then used for the next adsorption run. Langmuir and Freundlich isotherms were employed to fit the experimental data. Figure 3-3a shows the bromide removal properties of fresh SIAC which is perfectly predicted by the Freundlich model. However, for the second and third adsorption experiments, the Langmuir isotherm showed an improved fit to the

experimental data. This suggests that the sorption of Br^- onto SIAC is likely to involve precipitation reactions between the Ag^+ sites on the SIAC and Br^- species in the solution. Assuming the multilayer adsorption theory (Freundlich theory) for the prediction of fresh SIAC performance, as long as there is some Ag^+ available, the AgBr precipitation reaction is likely to occur and will continue until all available silver has reacted.



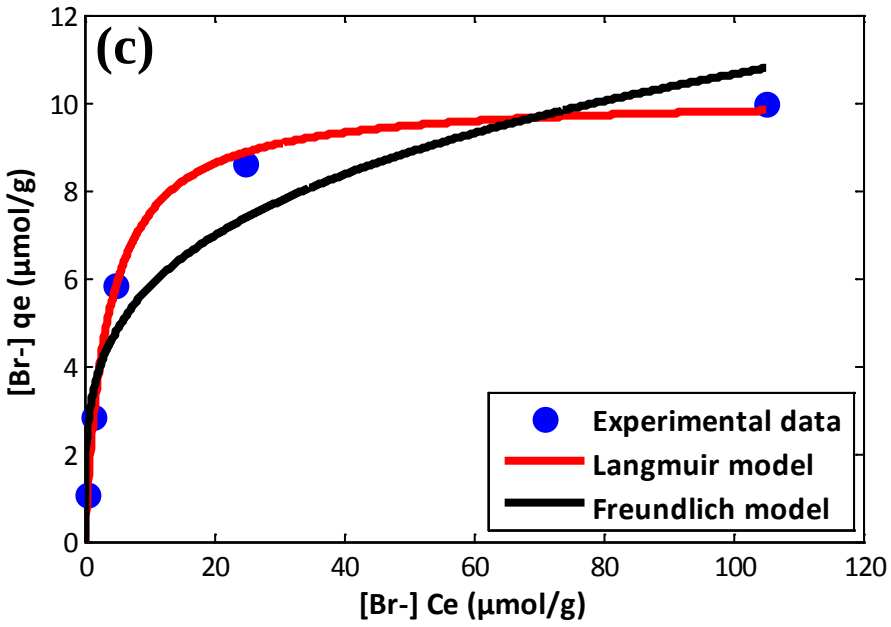


Figure 3-4: Three consecutive adsorption isotherms of the bromide uptake as a function of initial bromide concentration (1.25, 3.125, 6.25, 12.5 and 25 µM) using Norit SIAC at pH_0 6.5, (a) first, (b) second and (c) third run fitted by Langmuir and Freundlich models

The Langmuir theory which is largely based on the electrostatic chemisorption of adsorbates on the adsorbent surface is in better agreement with the third equilibrium data than the Freundlich theory. During the third equilibrium, where most of the silver sites on the SIAC are presumably in the form of AgBr, it is hypothesised that electrostatic interactions between the SIAC positively charged surface and the corresponding bromide anions induces the removal of Br^-. This confirms previous studies that silver-carbon adsorbents are highly efficient in the removal of bromide at concentrations relevant to drinking source waters (Sánchez-Polo et al. 2007; Gong et al. 2013; Watson et al. 2016; Chen et al. 2017). However, several other factors have to be taken into account before implementing adsorbents for selective removal of bromide, including the rate of bromide adsorption, leaching of silver from the adsorbent into the treated water and the impact of competing species such as natural organic matter (NOM) which are further discussed in following sections of this research.

Table 3-2: Results of adsorption isotherms fitting

	Langmuir model		**Freundlich model**	
	q_m	b	K	n
First Run	28.721	0.255	7.664	2.938
Second Run	16.306	0.269	4.585	3.446
Third Run	10.159	0.276	3.151	3.783

3.4.4 Bromide Removal Kinetics

The effect of contact time on bromide removal of Norit SIAC, representing the SIAC with the highest bromide removal capacity, is shown in Figure 3-5. Each plot of C_t (liquid-phase concentration per unit mass of SIAC) versus contact time can be divided into three stages. The fast bromide removal within initial 30 min (the first stage), thereafter, the uptake increases as time elapses from 30 to 120 min (the second stage) but with a slower rate. Finally (the third stage), there is no significant change in uptake after 120 min, which means that the removal of bromide through Norit SIAC has reached equilibrium.

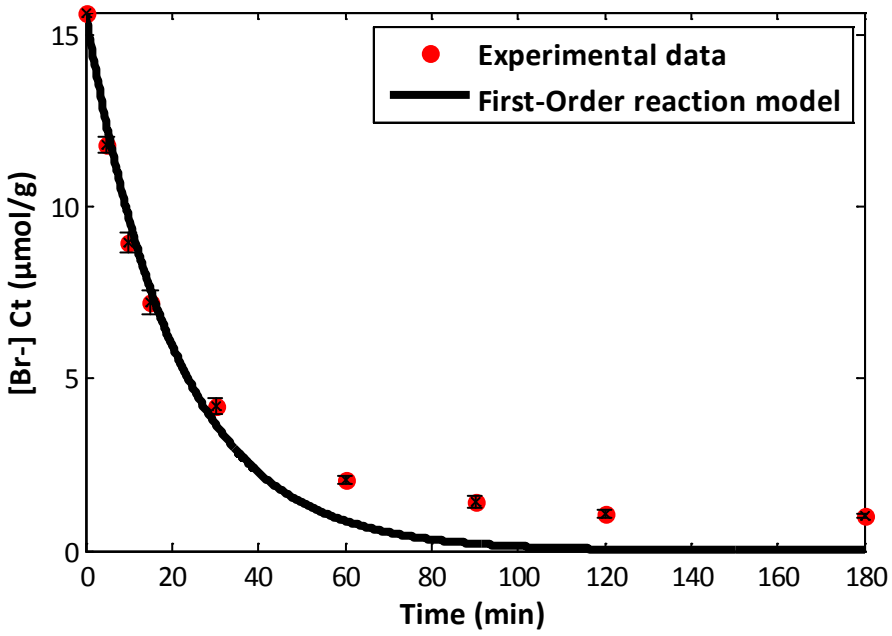


Figure 3-5: Bromide uptake behaviour of 400 mg of Norit SIAC during a 180 min batch experiment where the initial concentration of bromide in 500 mL ultrapure water was 1mg/L (12.5 µM) at pH_0 6.5

The results were analysed with the first-order rate equation:

$$[Br^-]_t = [Br^-]_0 \, e^{-kt} \quad (6)$$

where concentration of bromide ($[Br^-]$) and contact time (t) were measured experimentally while rate constant (k) was a fitted parameter. In the first stage, the bromide removal data fitted well with the first-order rate model. For the virgin SIAC, the accessible silver sites are vacant, leading to a fast bromide removal. At this stage, more than 66% of the dissolved bromide was removed in the first 30 minutes ($[Br^-]_{t=30min}$=4.2 μmol/g). Additionally, the greater concentration gradient between the bromide solution and SIAC surface would further accelerate the attractive forces between bromide from the liquid-phase and positively charged SIAC surface, causing the fast increase of uptake in initial stage. As the adsorption continues to the second stage (30 – 120 min), a difference (overestimation) between model and experimental bromide removal data in the 2nd and 3rd stages was observed. This may be attributed to the reduction of available adsorption sites for bromide on the SIAC. After 120 min (the third stage), no bromide was removed from the solution because the adsorption equilibrium was reached. Without the determination of the extent of silver leaching, these observations would not entirely support the previous studies speculating that precipitation in the form of silver-halide (e.g. AgBr) has to be taking place within the SIAC pores (heterogeneous precipitation) (Hoskins et al. 2002; Sánchez-Polo et al. 2007; Watson et al. 2016; Chen et al. 2017). The following reaction would be the precipitation of AgBr either on the surface of SIAC (solid-phase) or in solution:

$$Br^-(aq) + Ag^+(surf) \rightarrow AgBr \downarrow, \; K_{sp} = 5.2 \times 10^{-13} \quad (5)$$

Total silver measurement after 180 minutes revealed that more than 3 μmol/g of silver, compared to initial concentrations of total silver in SIAC (0.1 wt% or 13.6 μmol/g, either dissolved or precipitated), was detected in solution (data not shown). Taking into account the observed silver loss, it can be deduced that keeping the pH_{PZC} of SIAC above the pH of working solution, would not prevent silver from leaching into solution. Generally, the solution conditions that can affect the mobility of a metal are: pH, oxidation/reduction potential, anion/cation exchange, dissolution and precipitation (Stumm et al. 1996). Here, it is hypothesised that the leaching of Ag^+ is

mainly due to the decrease of pH from 6.5 to about 5 after 180 minutes. When the solution pH is decreasing, the protonation of SIAC surface can result in higher Ag^+ release into solution. Similar studies on silver leaching properties of Ag-incorporated adsorbents also confirmed that the variation in solution pH alters the Ag^+ stability on SIAC (Hoskins et al. 2002; Sánchez-Polo et al. 2007; Chen et al. 2017). However, in a real water sample, where water is buffered, solution pH may not be the only factor controlling the extent of silver leaching. Therefore, other interfering factors, and most importantly, natural organic matter, was further studied in this research.

3.4.5 Effect of NOM Surrogates on SIAC Bromide Removal Efficiencies

The bromide removal data for the Norit SIAC in contact with a range of synthetic bromide solutions (12.5, 25, 50 and 75 µM) containing 3.6 mgC/L of tannic acid (TA) and gallic acid (GA) are shown in Figure 3-6. Higher values for Br^- residuals were observed in the presence of GA compare to those of TA while the initial Br^- was elevated up to 75 µM. Therefore, it is apparent that the coexistence of GA molecules resulted in more interferences in removal of bromide through SIAC compared to that of TA.

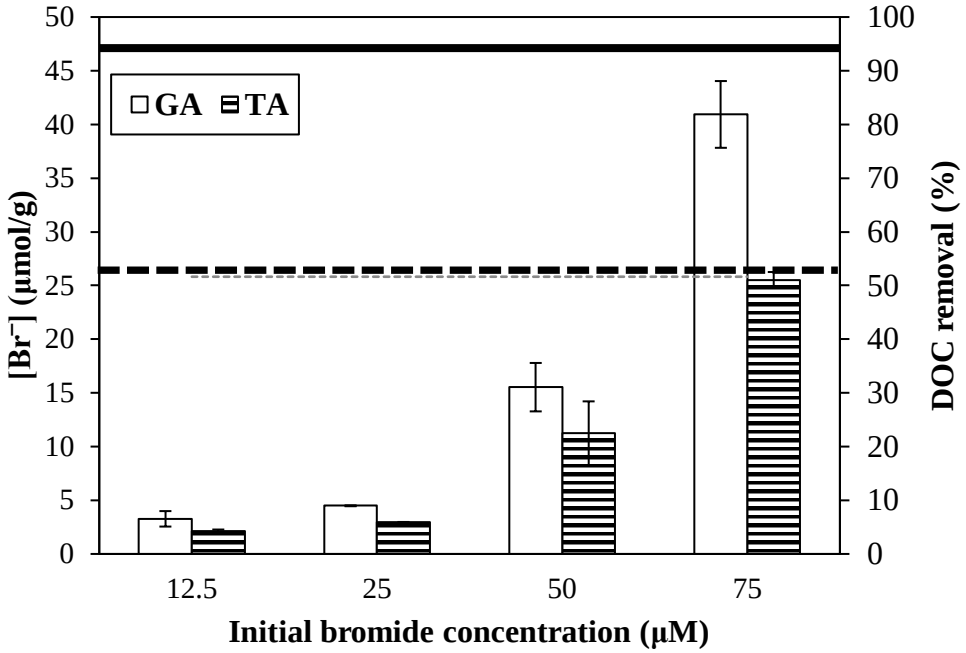


Figure 3-6: The bromide residual values after a 24 hours batch experiment at four different initial concentration of bromide (12.5, 25, 50 and 75 µM) and in presence of 3.6 mgC/L of GA (black) and TA (patterned) using 200 mg Norit added to the 200 mL solution at pH_0 6.5. An average of DOC removal for both of the TA (dashed line) and GA (solid line) is also plotted

At 12.5 µM of Br^-, where the initial concentration of bromide was lower than the total amount of available silver in SIAC (13.6 µmol/g), the bromide removal was reduced from above 97% in the absence of organics (Figure 3-2) to about 83 and 74% in the presence of TA and GA, respectively. Nevertheless, even at higher initial Br^- concentration, e.g. at 75 µM, an observable higher bromide removal was attained in the presence of TA (66%) compared to that of GA (45%). As shown earlier, when the initial concentration of bromide is higher than the total amount of available silver in SIAC, the bromide removal pathway is a combination of direct silver and bromide reaction (AgBr formation) and also the attractive electrostatic forces between SIAC and bromide in solution.

DOC removal data which are indicated with solid (GA) and dashed (TA) horizontal lines in Figure 6, reveals a significantly higher affinity of Norit SIAC towards GA than TA macromolecules. An average of 94% DOC removal was observed for GA containing bromide solutions. However, a significantly lower DOC removal efficiency of about 52%, was obtained in the case of TA inclusion in all Br^- solutions. This may be because the molecular weight of GA is approximately 10 times lower (170.12 g/mol) than that of TA (1701.19 g/mol) which could mean that smaller GA molecules are more likely to reach and occupy more of the available silver sites in SIAC porous structure (Ferro-García et al. 1998). Therefore, the enhanced removal of GA molecules may be correlated with the impeded removal of bromide through SIAC, predominantly at lower Br^- concentrations. It can also be concluded that a portion of silver is incorporated into smaller pores so that it cannot be reached by TA macromolecules.

3.4.6 Effect of NOM Surrogates on SIAC Bromide Removal Kinetics

In order to investigate the influence of contact time on the extent of Br^- removal in the presence of TA and GA organic model compounds, adsorption kinetics experiments were carried out over the course of 5 hours. The rate of bromide removal in the blank solution, without the presence of dissolved organics (DOC), was rapid within the first 30 minutes and only 6% of initial bromide remained in the solution after the 30 minutes (Figure 3-7). However, in the solutions containing organic matter (TA and GA organics) there was a significant deterioration in the bromide removal efficiency

of SIAC. The values for bromide residual were significantly increased to 27 and 30% in the presence of TA and GA organics, respectively (Figure 3-7). Upon increasing contact time, the extent of Br^- removal in DOC-containing bromide solutions increased consistently and reached its maximum (above 95%) after 300 minutes. However, in contrast to the DOC-containing solutions, the maximum bromide removal efficiency in the blank solution was reached after only 120 minutes and remained relatively unchanged for the rest of the experiment.

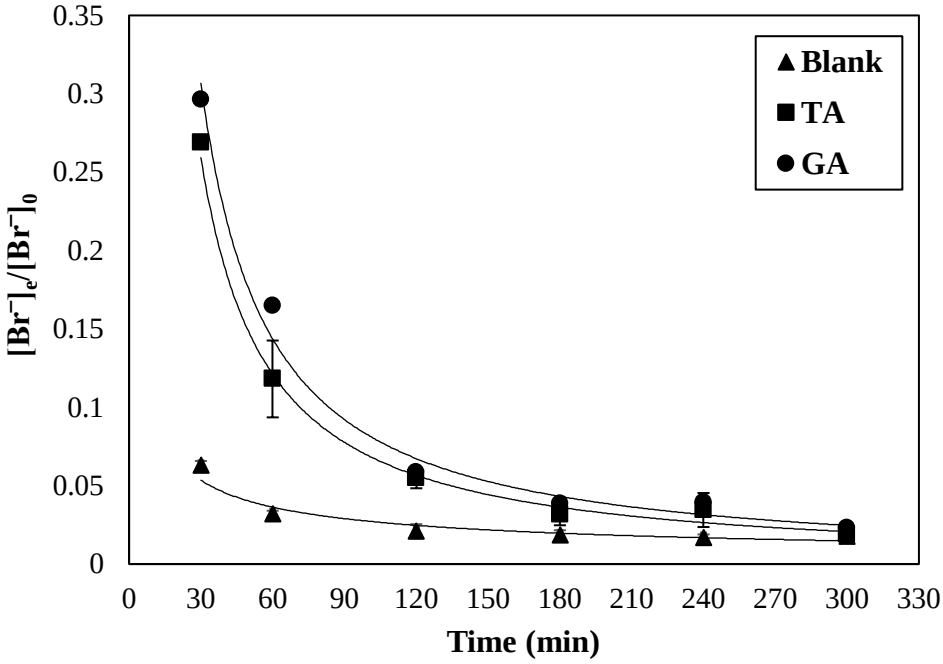


Figure 3-7: Bromide uptake behaviour of 200 mg Norit SIAC in three five-hour isothermal batch experiments conducted at 6.25 µM initial concentrations of bromide without the presence of organics (Blank) and also in the presence of 3.6 mgC/L of Tannic acid (TA) and Gallic acid (GA) in 200 mL solution at pH_0 6.5

These results showed that the coexistence of TA and GA organic model compounds led to a slower bromide removal However, the overall bromide removal capacity remained unchanged after continuing the experiment for a longer contact time. The main reason for the similar bromide removal capacities observed in all experimental conditions is unclear. However, the slower bromide removal rates observed in the presence of TA and GA compared to that of blank solution was probably caused by inactivation of available silver incorporated into SIAC. In order to further investigate the mechanisms of bromide removal in presence of TA and GA organic model compounds, the rates for the silver leaching along with the corresponding DOC removal results were plotted in Figure 3-8 and 3-9, respectively. The extent of silver

leaching over time for the blank and the two DOC-containing bromide solutions is shown in Figure 3-8.

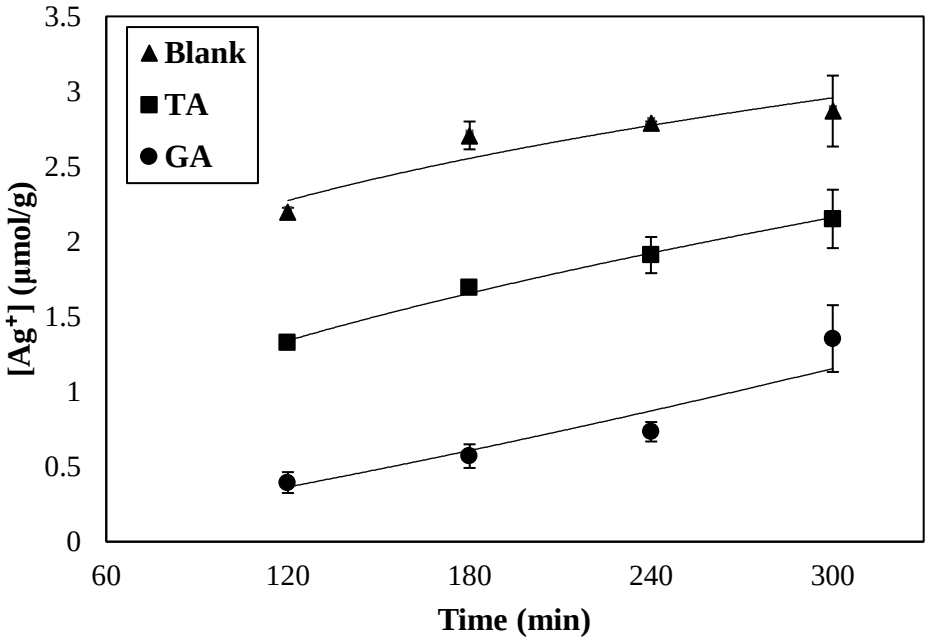


Figure 3-8: The silver leaching behaviour of 200 mg Norit SIAC in three five-hour isothermal batch experiments conducted at 6.25 µM initial concentrations of bromide without presence of organics (Blank) and also in presence of 3.6 mgC/L of Tannic acid (TA) and Gallic acid (GA) in 200 mL solution at pH_0 6.5

The silver leaching values for blank bromide solution (containing no organic matter) were higher than those for TA and GA containing solutions, with the minimum silver leaching being achieved in the presence of GA. For example, the silver leaching increased from 0.4 up to 1.3 µmol/g of Ag^+ during the last three hours of the experiment in presence of GA. In comparison, in the absence of organics, the Ag^+ leaching increased from 2.2 to 2.9 µmol/g. This supports the above mentioned hypothesis that the presence of organics can inactivate and block some Ag^+ sites incorporated into SIAC. For GA, the extent of silver leaching was relatively lower compared to that in TA containing bromide solutions, with a maximum of 2.1 µmol/g after five hours experiment. The higher amount of silver leaching from SIAC in the presence of TA molecules may also be qualitatively consistent with its corresponding lower bromide and DOC removal data displayed in Figures 3-7 and 3-9.

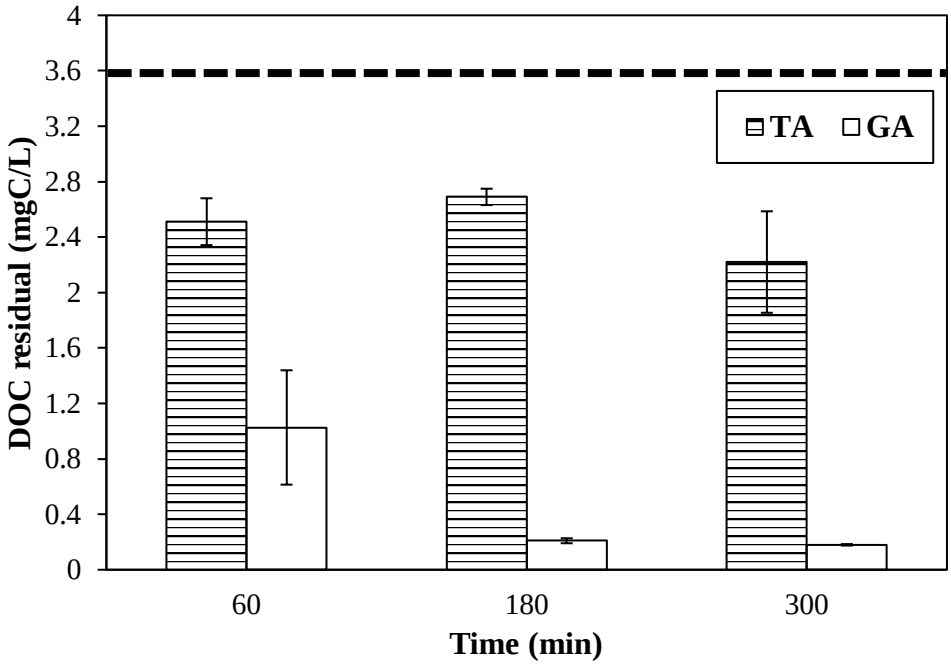


Figure 3-9: DOC residual in the 200 mL samples containing 3.6 mgC/L of initial dissolved organics (dashed line) sourced from Tannic acid (TA) and Gallic acid (GA) treated by 200 mg Norit SIAC at pH_0 6.5 as a function of time.

The DOC uptake as well as silver leaching behaviours observed in the presence and the absence of TA and GA were also different, suggesting that no single factor appears to be responsible for the bromide removal process. During the treatment of solution free of organics by SIAC, two possible mechanisms for the removal of bromide can be suggested: (i) direct reaction of silver and bromide and precipitation of silver bromide (AgBr) on SIAC surface (ii) silver leaching to liquid-phase and consequently reacting with bromide so that silver bromide precipitates are formed in the solution. In the presence of GA small molecules, the Ag^+ active sites are blocked and inactivated so that AgBr formation will likely occur until all available Ag^+ have reacted. Unreacted bromide residuals will then be removed (at a slower rate) through the electrostatic chemisorption onto the SIAC reactive sites. The impact of TA on the performance of SIAC was found to be different from GA, perhaps due to its 10 and 20 times higher molecular weight and solubility (Liu et al. 2012). The rates of DOC residuals depicted in Figure 3-9 showed significantly higher adsorption capacities of SIAC for GA compared to TA. A maximum of 95% of DOC removal was obtained during the SIAC treatment of GA containing solution, while this value was reduced down to only 40% in presence of similar DOC concentration of TA. Compared to GA, the TA larger molecular weight and thus higher steric hindrance, would possibly result

in a limited access to the smaller pores of SIAC (Liu et al. 2012). In contrast to GA, TA molecules had more deteriorating impact on the extent of silver leaching from SIAC. Figure 3-8 shows that the released silver is two times higher for TA compared to GA. During the 5 hours of experiment, the Ag^+ leaching from the TA containing bromide solution was ranged from 1.3 to 2.1 μmol/g, which was in an average, higher and lower compared to that in GA and blank Br^- solutions, respectively. Compared to GA, the larger number of phenolic functional groups capable of complexing with Ag^+ can possibly be the main reason for the higher extent of silver leaching in TA containing solution. However, due to the extremely low solubility products for AgBr ($K_{sp} = 5.2 \times 10^{-13}$), the tendency for the conversion of Ag-TA complexes to the formation of AgBr might be increased, towards the end of experiment. Therefore, a large portion of bromide is precipitated in solution (unfavourable) instead of being attached to the SIAC surface (favourable). Overall, it can be deduced that the coexistence of dissolved organics would alter the bromide removal pathways through SIAC. However, the presence of smaller organic model compounds such as GA, could block the SIAC pores and also would possibly directly inactivate Ag^+ sites.

3.4.7 Effect of SRHA and SRFA on Bromide Removal and Silver Leaching Properties

The interfering effect of coexisting SRHA and SRFA NOM isolates on the extent of bromide removal through Norit SIAC was investigated for various initial DOC concentrations (1, 2 and 4 mgC/L). Figure 3-10a and b compares the simultaneous effects of NOM type and concentrations on bromide removal capacity for 0.8 g/L of Norit SIAC, representing the highest performance, after 30 and 180 minutes. At 30 minutes, the bromide residual increased with increasing DOC concentration (Figure 3-10a). The amount of bromide removed in the blank solution was about 8.3 μmol/g (66% removal) which was higher than the corresponding values in presence of NOM isolates. However, there was not much differences between the samples containing the two NOM isolates. Interestingly, a relatively lower bromide removal capacity was observed for the blank solution with increasing contact time (180 minutes). These observations were not consistent with previous studies reporting on significant reduction in the bromide removal efficiency in the presence organic molecules in the bromide solution (Gong et al. 2013; Chen et al. 2017).

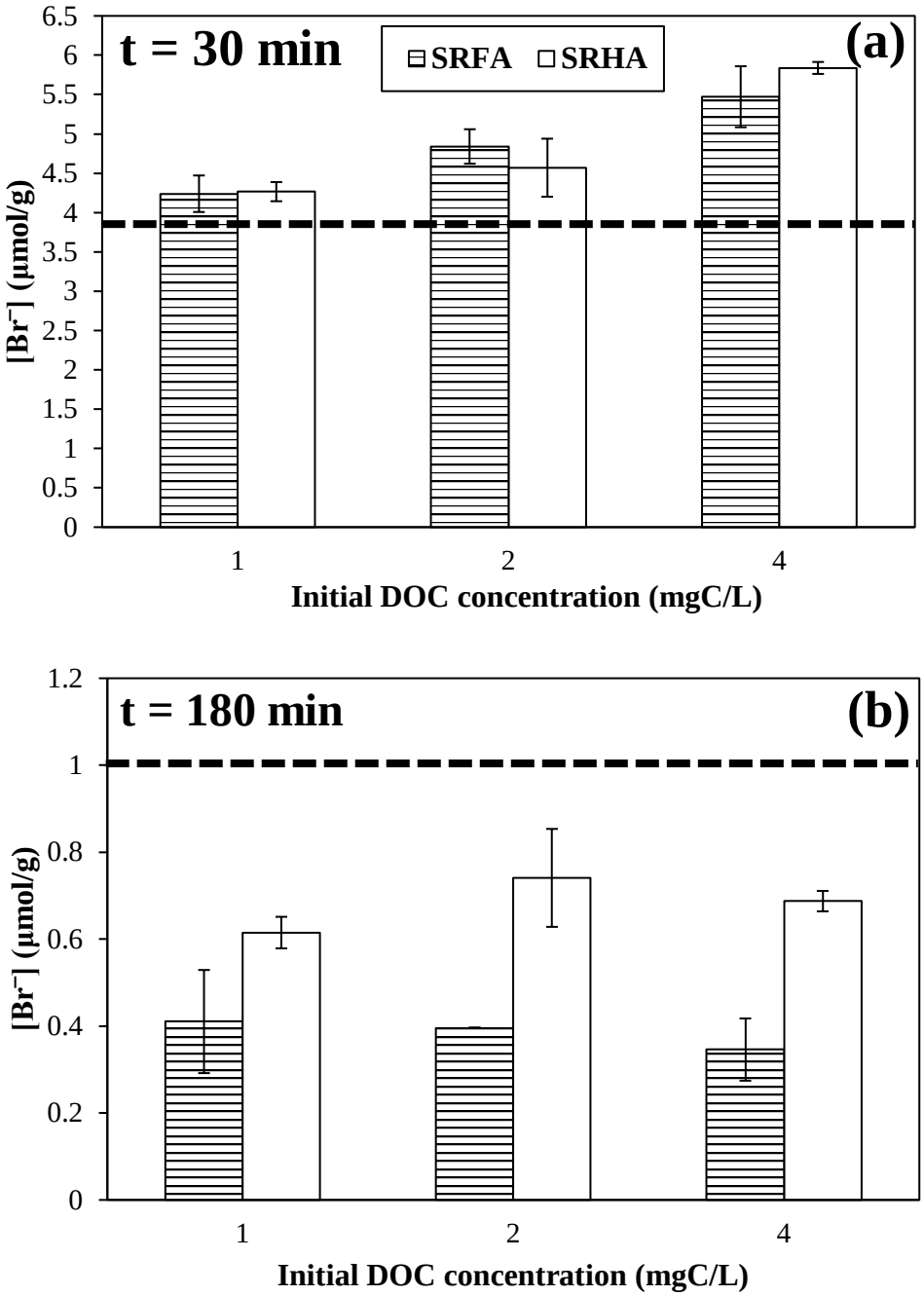


Figure 3-10: The bromide residual values after (a) 30 minutes and (b) 180 minutes batch experiment at three different initial concentration of SRHA and SRFA NOM isolates (1, 2 and 4 mgC/L) and in presence of 12.5 µM of bromide using 400 mg Norit added to the 500 mL solution at pH_0 6.5. An average of bromide residual for a blank experiment is also plotted (dashed line), where no organics is added to the solution

The DOC removal obtained for both of SRHA and SRFA did not exceed 6 and 12%, respectively (data not shown), thus the pore blockage mechanism by NOM molecules which is proposed in the literature, may not be the only factor reducing the bromide

removal efficiency. Therefore, to better describe the predominant mechanism affecting the bromide removal variations in the presence of NOM isolates, the silver leaching behaviours of SIAC was investigated in the presence and in the absence of Br^- in NOM-containing solutions. The extent of silver leaching from the Norit SIAC as a function of initial SRHA and SRFA concentrations is shown in Figure 3-11.

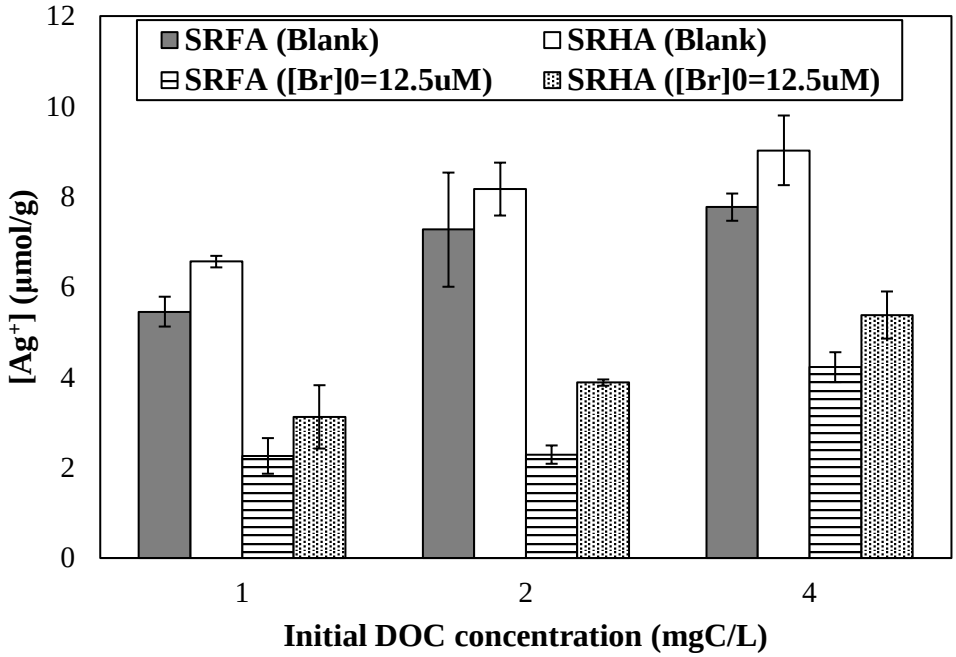


Figure 3-11: The silver residual values after 360 minutes batch experiment at three different initial concentration of SRHA and SRFA NOM isolates (1, 2 and 4 mgC/L) and in presence and in the absence of 12.5 µM of bromide using 400 mg Norit added to the 500 mL solution at pH_0 6.5.

According to these observations, the significantly higher silver leaching values were associated with blank NOM-containing solutions with no Br^- interferences. It has been reported that there is a high affinity in SRFA and SRHA for Ag^+ due to the presence of electron donating groups containing oxygen (e.g. carboxylic acids and phenols) (Settimio et al. 2015). Therefore, one possibility describing the silver leaching results can be attributed to the release of silver from SIAC in the form of Ag^+–NOM complexes. From the silver leaching results shown in Figure 3-11, it can be deduced that the bromide removal was taken place through a combined pathway. Part of the bromide in the liquid-phase directly reacts with the available silver incorporated into SIAC so that the formation of AgBr precipitates would reduce the extent of silver leaching in to solution. Alternatively, the rest of the bromide will be removed by aqueous-phase precipitation of Ag^+ which has leached into solution. Moreover, for

both types of NOM isolates, the silver leaching became more significant with the increase in initial DOC concentration from 1 to 4 mgC/L. However, the extent of silver leaching is observed to be relatively higher in the presence of SRHA compared to those of SRFA. A possible mechanism explaining the latter is that the SRHA molecules contain an approximately two times higher nitrogen content (e.g. amines, amides and heterocyclic nitrogens) compared to those of SRFA, while they both have a similar carbon content. This can be attributed to the increased the ratio of N/C in NOM molecules so that the affinity of NOM molecules for silver sites of the SIAC would be increased (Cawley et al. 2013; Yoo et al. 2016)

3.4.8 Implications for the Bromide Removal from a Real Water Matrix

A real water matrix from a bore in Western Australia with specifications given in Table 3-1 was employed for the assessment of two types of SIAC (WT400 and Norit) and the GAC for their bromide and DOC removal performances. No reduction in bromide concentration was detected when using WT400 SIAC and GAC during 180 minutes. Whereas for DOC removal, both WT400 SIAC and GAC were performing relatively efficiently, with DOC residual values of 1.31 and 1.16 mgC/L, respectively (above 60% removal efficiency). On the other hand, Figure 3-12 compares the Br^-, DOC and $SUVA_{254}$ values of real water sample before and after the treatment with Norit SIAC.

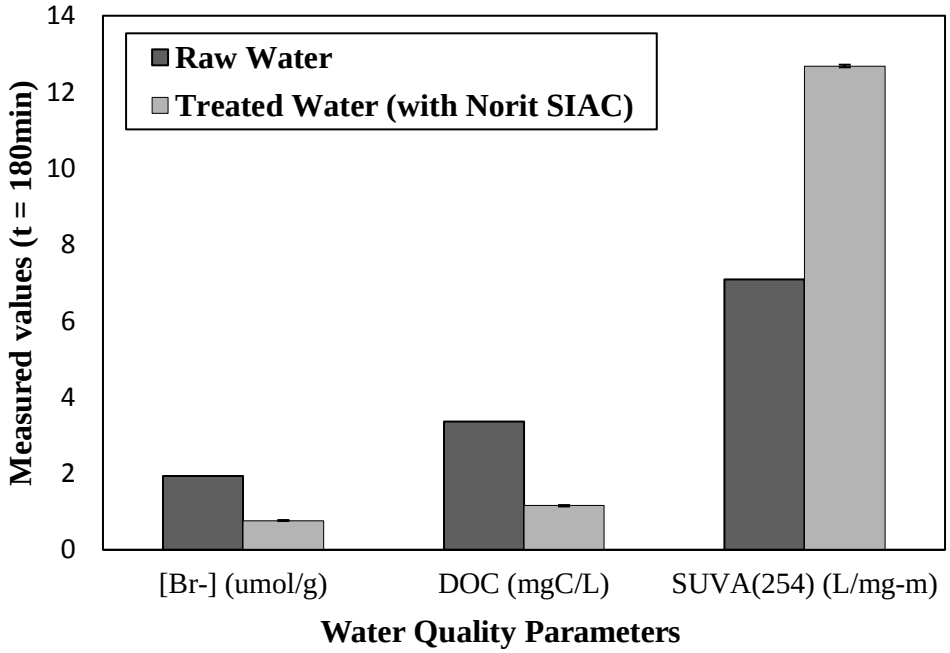


Figure 3-12: The initial (black) and residual (grey) values after 180 minutes batch experiment using 200 mg Norit added to the 200 mL solution at pH_0 7.1.

According to these observations, Br^- concentration was reduced from 2 µM to 0.7 µM, indicating a removal efficiency of 60%. Additionally, DOC also decreased by 65%, where the 3.7 mgC/L of initial DOC in raw water sample was lowered to about 1.2 mgC/L after 180 minutes. Unlike the Br^- and DOC residuals in treated water, the $SUVA_{254}$ value increased after the treatment with Norit SIAC. In fact, the extent of aromaticity in DOC residual, measured by $SUVA_{254}$, was not removed during the SIAC treatment. This result would suggest that the Norit SIAC has low affinity for the adsorption of aromatic fractions of NOM molecules. Previous studies also showed that NOM molecules containing lower aromaticity and consequently higher hydrophilic fractions induced higher binding capacities and affinities for Ag^+ compared to the corresponding hydrophobic NOM with higher degree of aromaticity (Yoo et al. 2016).

3.5 Conclusions

This study confirmed that silver-carbon adsorbents are highly efficient in the removal of bromide at concentrations relevant to drinking source waters and that fresh GAC also appears to remove appreciable concentrations of bromide. However, several other factors that have not been considered in previous similar studies such as kinetics of bromide adsorption and the leaching of silver from the SIAC into the treated water,

were assessed. More than 66% removal of bromide was observed after the first 30 minutes in water free of organics, where no other interfering species existed. However, as the adsorption proceeded to 180 min, the rate for the bromide removal slowed down. This is attributable to the reduction of available adsorption sites on SIAC. Langmuir and Freundlich isotherms were also employed to study bromide adsorption. It was found that the bromide removal properties of fresh SIAC were perfectly described by using the Freundlich adsorption model. However, for the second and third adsorption experiments, the Langmuir isotherm showed an improved fit to the experimental data. This suggests that the sorption of Br^- onto SIAC is likely to involve co-precipitation reactions between the Ag^+ sites on the SIAC and Br^- species in the solution. Assuming the multilayer adsorption theory (Freundlich theory), the AgBr precipitation reaction is likely to occur and will continue until all available silver has reacted. Despite the superior bromide removal achieved in the absence of organic and inorganic interferences, interesting results were obtained for the SIAC treatment of a real water samples containing 0.155 and 3.37 mg/L of initial bromide and DOC, respectively. It was observed that the bromide and DOC removal efficiency were both above 60% after 180 min of agitation. However, the $SUVA_{254}$ value indicating the extent of aromaticity in the natural organic matter residual, was found to be increased after SIAC treatment. These results along with DOC uptake results obtained for TA and GA organic molecules would suggest that SIAC has low affinity for the adsorption of aromatic fractions of NOM molecules.

Chapter 4

Effect of Silver-impregnated Activated Carbon Preconditioning on Silver Leaching and Bromide Removal Properties

4.1 Abstract

In the previous chapter, silver impregnated activated carbon (SIAC) has been found to be effective in removing bromide from synthetic and real water samples. However, there are still uncertainties regarding its silver leaching properties, and strategies for the prevention of silver leaching have remained elusive. The focus of this Chapter is therefore on the evaluation of one type of commercially available SIAC for its ability to remove bromide while minimising silver leaching from the material. Both synthetic and real water matrices were tested. The study results suggest that the extent of silver incorporation is not the only factor determining the efficiency of SIAC for bromide removal applications. Depending on solution pH, it was found that modification of the SIAC surface (shifting the point of zero charge pH (pH_{PZC})) can potentially result in additional bromide removal while minimising the extent of silver leaching from SIAC. To mitigate silver leaching, the SIAC was preconditioned at high pH (pH 10.4). To better understand the mechanism of silver leaching from SIAC, eight preconditioning environments, i.e. variable pH and ionic strength (IS) were tested for a fixed amount of SIAC and two preconditioning environments were selected for a more detailed investigation. It was found that preconditioning at pH 10.4 and also in 1 mM sodium perchlorate did not deteriorate the capacity of SIAC to remove bromide, but that it decreased the release of silver in the form of ionic silver (Ag^+), silver bromide (AgBr) and silver chloride (AgCl) by 40%. The assessment of preconditioned SIAC in a natural water matrix showed a similar bromide removal capacity compared to that of pristine SIAC. However, SIAC preconditioned at pH 10.4 had almost three-times lower silver leaching compared to pristine SIAC. These results suggest that preconditioned SIAC has the potential to be effective for bromide removal with minimised silver leaching from drinking source water in a long-term field application.

4.2 Introduction

Naturally occurring bromide in drinking water source creates a multitude of problems for water utilities (Heeb et al. 2014; Allard et al. 2015). When water is disinfected by chlorine, bromide is rapidly converted to hypobromous acid (HOBr) (Kumar and Margerum 1987) which reacts in an analogous way to chlorine (HOCl). However, reactions involving HOBr are generally several orders of magnitude faster than those of HOCl (Criquet et al. 2012, 2015). Furthermore, the toxicity of halogenated

disinfection by-products (DBPs) is generally increased in chlorinated waters containing bromide, mainly due to the fact that brominated DBPs (Br-DBPs) are more toxic than chlorinated DBPs (Cl-DBPs) (Flury et al. 1993). In addition, bromide can be considered as a catalyst in many of the reactions involving chlorine in drinking water supply systems (Duirk et al. 2008; Criquet et al. 2012). In addition to the formation of disinfection by-products, bromide in source water causes water quality problems including increased disinfectant loss (Sedlak et al. 2011) and higher concentrations of odorous brominated compounds (Acero et al. 2005; McDonald et al. 2013). The presence of bromide can also be advantageous e.g., it can expedite the oxidation of manganese (II) to MnO_2 which is removed by a filtration process and increase the rate of iodide oxidation to iodate minimising the formation of toxic I-DBPs (Allard et al. 2013; Allard et al. 2015; Criquet et al. 2012). However, Br-DBPs and organic bromine, typically measured as adsorbable organic bromine (AOBr), have recently been reported as the dominant halogenated species after chlorination of ground- and surface- raw waters containing high concentrations of bromide (Tan et al. 2016; Langsa et al. 2017). In addition, during disinfection with ozone, bromide can form bromate, a regulated DBP and suspected carcinogen. Bromide is oxidised to bromate via a complex series of mechanisms (von Gunten 2003) and its formation may be minimised by pH control (Allard et al. 2013). However, the best way to avoid the formation of bromate is to remove bromide prior to the final disinfection step.

There is currently no economically viable method for the selective removal of bromide from drinking water sources. Tight membrane processes such as reverse osmosis and nanofiltration are the only commercially available methods which can effectively remove halides to very low levels (Harrison et al. 2007; Khan et al. 2005). However, these are not considered economical where the primary objective is bromide reduction due to issues such as susceptibility to fouling and scaling, high energy consumption, short lifespan and high cost. These shortcomings, and the fact that membrane processes actually treat water to a much higher purity than required, have led to a need for alternative methods for bromide removal. Studies investigating the selective removal of bromide during drinking water treatment processes have mainly focused on adsorption techniques which can be readily retrofitted to existing conventional water treatment processes for minimal capital and operational cost. Magnetic ion-exchange resins (Hsu et al. 2010), aluminium chloride salt (Ge et al. 2007, 2008),

mixed metal hydrous oxides (Chubar et al. 2005; Chubar 2011) and layered double hydroxides have been proposed as adsorbents for bromide removal (Echigo et al. 2007; Chitrakar et al. 2008; Lv et al. 2008). Activated carbon (AC) materials have conventionally been effective for the sorption of organic carbon, but several recent studies reported that AC materials have low selectivity for bromide uptake from natural waters (Hoskins et al., 2002; Kristiana et al., 2011; Watson et al., 2016).
Silver impregnated activated carbon (SIAC) materials are known for their excellent antibacterial properties in water disinfection processes and have been utilised for this purpose for a number of years (Ortiz-Ibarra et al. 2007; Bandyopadhyaya et al. 2008). Due to the high affinity of halide ions towards silver, recent research has shown that SIAC can also be a promising alternative for the removal of halides from water (Hoskins et al. 2002; Gong et al. 2013; Watson et al. 2016).

Silver halides are very insoluble in water, with their solubility constants (K_{sp}) decreasing in the order of the occurrence of their respective halide ion in natural waters: AgCl ($K_{sp} = 2.8 \times 10^{-10}$) > AgBr ($K_{sp} = 5.2 \times 10^{-13}$) > AgI ($K_{sp} = 8.5 \times 10^{-17}$). Hence, even in the presence of high concentrations of chloride, i.e. 100-fold higher than bromide and iodide, these minor ions can be selectively removed from solution using silver. However, the direct addition of silver, as in silver salts, to water is not practical due to the difficulties in removing very fine silver halide particulates (AgX) from water, not to mention ethical and regulatory hurdles surrounding the prospect of adding silver directly to water supplies (the Australian Drinking Water Guideline maximum value for silver is 0.1 mg/L). Therefore, a form of silver that is immobilised, for example within a filter medium, would be a potential solution for the removal of undesirable halides in a water treatment process.

It has been found that SIAC (1.05 wt % silver) can be an efficient adsorbent in removing iodide (I^-) from solution, where silver content, total iodide concentration, and solution pH were identified as the controlling factors (Hoskins et al. 2002). If the molar concentration of silver is greater than that of iodide ($M_{Ag,SIAC} > M_{I,Total}$), precipitation of silver iodide is the dominant removal mechanism and excess unreacted silver would be leached into solution, with the amount leached increasing with decreasing pH (Hoskins et al. 2002). In another study, silver-doped carbon aerogels (Ag-aerogel) were successfully synthesized and assessed for the simultaneous removal

of bromide and iodide from synthetic and natural waters (Sánchez-Polo et al. 2007). This study showed that the Ag-aerogels have high bromide uptake capacity (above 90%), while the addition of excess chloride (Cl^-, 40 mg/L) reduced the capacity to adsorb bromide by 36%. However, the extent of silver leaching was not determined in this research, where relatively high concentrations of silver (4 – 10 wt% silver) compared to those of bromide (0 – 10 µM) were used (Sánchez-Polo et al. 2007).

A recent study compared the efficiency of a commercially available SIAC with 0.1wt% silver and its equivalent unimpregnated activated carbon for the simultaneous removal of bromide, iodide and NOM from water (Watson et al. 2016). Their results showed that the combination of enhanced coagulation (EC) with SIAC treatment can remove more than 95% of bromide, while EC coupled with unimpregnated activated carbon removed only 26% of bromide. However, the authors stated that further investigation towards the understanding of silver leaching mechanisms is required in order to apply this type of SIAC to bromide removal in a large-scale water treatment plant (Watson et al. 2016). A more recent study reported on the development of SIAC preparation to enhance removal of Br^- from natural waters so that the formation of brominated trihalomethanes (THMs) is controlled (Chen et al. 2017). Although the silver impregnation process was identified as one of main factors affecting the Br^- removal efficiency, no quantification on the extent of silver leaching from the SIAC was reported.

Therefore, one of the main objectives of this research was to better understand the mechanisms of silver leaching from SIAC under typical water treatment conditions in order to develop approaches to minimise silver leaching during bromide removal applications. In this study, several factors that govern the practicalities of the use of SIAC for bromide removal, including the kinetics of bromide adsorption and, in particular, the leaching of silver from the SIAC to the treated water, were investigated. The SIAC was first conditioned in order to reduce silver leaching based on the SIAC surface chemistry (i.e. point of zero charge pH). Then, the reaction pathways of the silver and bromide reactions were determined for both pristine and conditioned SIAC. In the last step, the bromide removal and silver leaching properties of SIAC were examined in a real water sample to identify the most important interferences from components of a natural water matrix.

4.3 Materials and Methods

4.3.1 Chemical, Reagents and Analytical Methods

Silver nitrate ($AgNO_3$ AR grade, ≥99.5%) was obtained from Rowe Scientific Pty Ltd. Sodium bromide (NaBr ReagentPlus®, ≥99%), potassium nitrate (KNO_3 ACS reagent, ≥99.0%), sodium perchlorate ($NaClO_4$ ACS reagent, ≥98.0%) were purchased from Sigma-Aldrich. All other reagents used including sodium chloride (NaCl), sodium hydroxide (NaOH), nitric acid (HNO_3, 70%) and hydrochloric acid (HCl, 34%) were supplied by Ajax Finechem Pty Ltd. These were of analytical reagent (AR) grade purity and were used without further purification. Ultrapure water produced by an ELGA water purification system (resistivity of 18.2 MΩ.cm) was used throughout this study for the preparation of reagents and solutions unless otherwise indicated. Norit AG grade silver impregnated, granular activated carbon with 18×40 mesh size (0.42-1.00 mm) and nominal silver content of 0.1wt% and total surface area (S_{BET}) equal to 1050 m^2/g was provided by Cabot Norit, Amersfoort, The Netherlands. A real water matrix from a groundwater bore in Western Australia with the following water quality parameters was used in this study; [SO_4^{2-}] = 35 mg/L, [HCO_3^-] = 180 mg/L, [Cl^-] = 570 mg/L, [Br^-] = 1.8 mg/L and [DOC] = 1.6 mgC/L. The total silver concentrations in solutions were measured using a Varian Model SpectrAA 50 flame atomic absorption spectrophotometer (AAS) with a nominal limit of detection (LOD) of 0.02 mg/L of Ag. Bromide, chloride and nitrate concentrations were measured in a single method using a Dionex ICS 3000 ion chromatography system with a Dionex IonPac AS9-SC (4.0 mm × 250 mm) analytical column, where the detection limit was 5 µg/L. The pH of the solution was measured using a Hach 40d pH meter equipped with PHC101 electrode. In order to determine the point of zero charge pH (pH_{PZC}) of SIAC, the pH was adjusted by addition of NaOH (10 mM) or HNO_3 (10 mM) to sodium nitrate ($NaNO_3$: 50 mL of a 0.01 M solution). SIAC (0.15 g) was added to each of the different pH solutions and the solutions were agitated for 72 h (Putra et al. 2009). The pH_{PZC} was estimated to be 7.2 ± 0.1.

4.3.2 SIAC Washing and Pretreatment

In order to remove fine particulates and water soluble impurities, SIAC particles were thoroughly washed 15 times with ultrapure water until no further turbidity was observed in the washing water. Dried SIAC (30.00 g) was weighed into a clean beaker

and was then rinsed in ultrapure water (200 mL) followed by ultrasonication for 5 min at ambient temperature. This was necessary to ensure loose silver-carbon fines were removed from the SIAC porous structure. Therefore, 15 times washed SIAC was used throughout this study unless otherwise indicated. The resulting SIAC particles were then dried overnight at 110 °C for further use. To evaluate the impact of washing on the chemical properties of the conditioned SIAC, samples were taken from the waste washing water after the first, second, third, tenth and the last washing step. The samples were then filtered through a 0.22 µm syringe filter and analysed for silver, chloride and nitrate. The 15 times washed SIAC, (called pristine SIAC in this manuscript), was further treated under various pH and ionic strength conditions. The pH and ionic strength values for the conditioning solutions were adjusted using sodium hydroxide (NaOH; 100 mM) and sodium perchlorate ($NaClO_4$; 1 M), respectively.

4.3.3 Batch Adsorption Studies

Batch adsorption tests were carried out by adding dried SIAC samples (0.40 g) to synthetic water samples (500 mL). Lovibond jar testing apparatus with 6 stirring places equipped with a water bath was used for the isothermal kinetic and equilibrium studies at 30 ± 0.5 °C with agitation speeds of 50, 150 and 200 rpm. In order to compare the ion uptake and leaching capacity of the SIAC for all experiments, the following correction factor was used:

$$C_t = \frac{V_L}{m_A}(C_{t,ins}) \qquad (4.1)$$

where C_t (µmole/g) is the liquid-phase concentration per unit mass of SIAC, $C_{t,ins}$ (µmole/L) is the liquid-phase concentration read by instrument, V_L (L) is the total volume of solution and m_A (g) represents the mass of SIAC. No buffer solution was used for the purpose of pH adjustment so that interferences by coexisting ions could be prevented. The pH values were, therefore, monitored during the experiments.

4.4 Results and Discussion

4.4.1 Optimal Stirring Rate for the Bromide Removal Using Pristine SIAC

In general, a higher stirring rate can minimise the influence of film mass transfer resistance in the vicinity of the adsorbent surface (Levenspiel 1999). However, it has been reported that the SIAC surface can intensify the oxidative dissolution of silver presumably due to the high concentration of oxygen available in the pores of the activated carbon (Hoskins et al. 2002). Therefore, in this study, the trade-off between bromide removal and silver leaching at various agitation speeds was evaluated to determine an optimal stirring rate for batch experiments (i.e. highest bromide removal and lowest silver leaching). For this purpose, the kinetics of silver leaching were determined at 50, 150 and 200 rpm in ultrapure water in the absence of bromide. This range was chosen based on preliminary bromide uptake and silver leaching tests which showed that the adsorption properties of SIAC were not influenced by stirring rates above 200 rpm. Although the amount of silver leaching to the solution increased with stirring time, no significant variation in silver concentration was observed with increasing stirring rate (Figure 4-1).

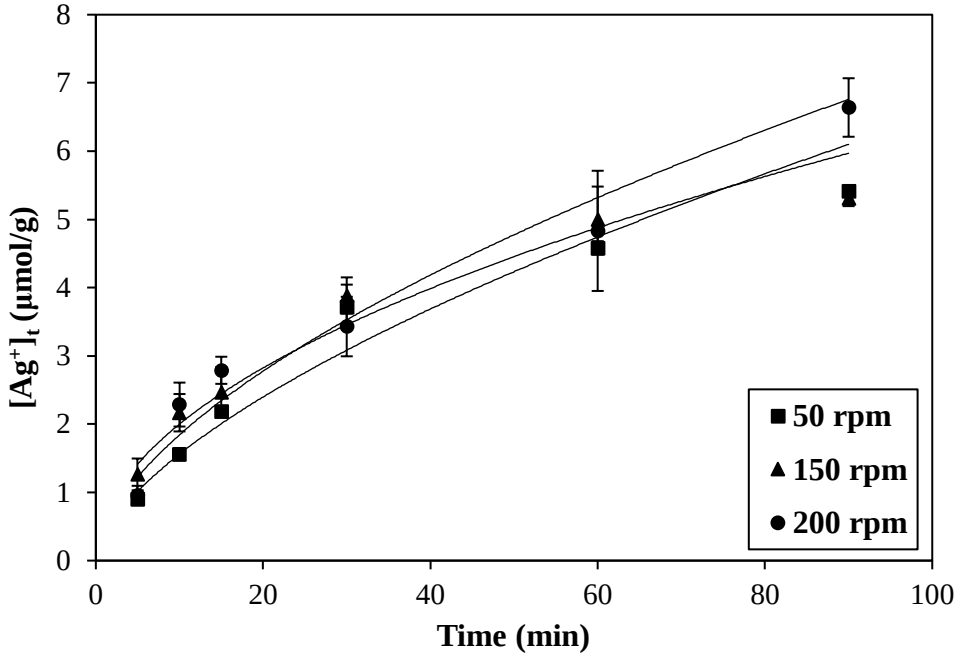


Figure 4-1: Effect of stirring rate on silver leaching from pristine SIAC.

Under stagnant conditions (zero rpm for 30 minutes) the amount of silver leached was negligible (i.e., < 0.02 mg/L). In a complementary experiment, the effect of stirring rate and time on the bromide removal capacity of SIAC was evaluated. The highest

bromide removal capacity was achieved at 150 rpm, where more than 90% of bromide was removed after 90 min of continuous agitation, while the lowest efficiency was observed for a stirring rate of 50 rpm (Figure 4-2).

At low stirring rate (50 rpm), it is proposed that a concentration gradient between the SIAC surface and the bulk solution builds-up. This slightly slows down the bromide access to the SIAC surface which is thought to be the main reason for the lower bromide uptake. At 200 rpm and above, the silver clusters within the carbon are possibly damaged and detached from the carbon due to the high turbulence intensity. High turbulence would also hinder the attachment of bromide on the adsorbent, which would consequently slightly minimise bromide uptake capacity from 94 to 86% at 150 rpm.

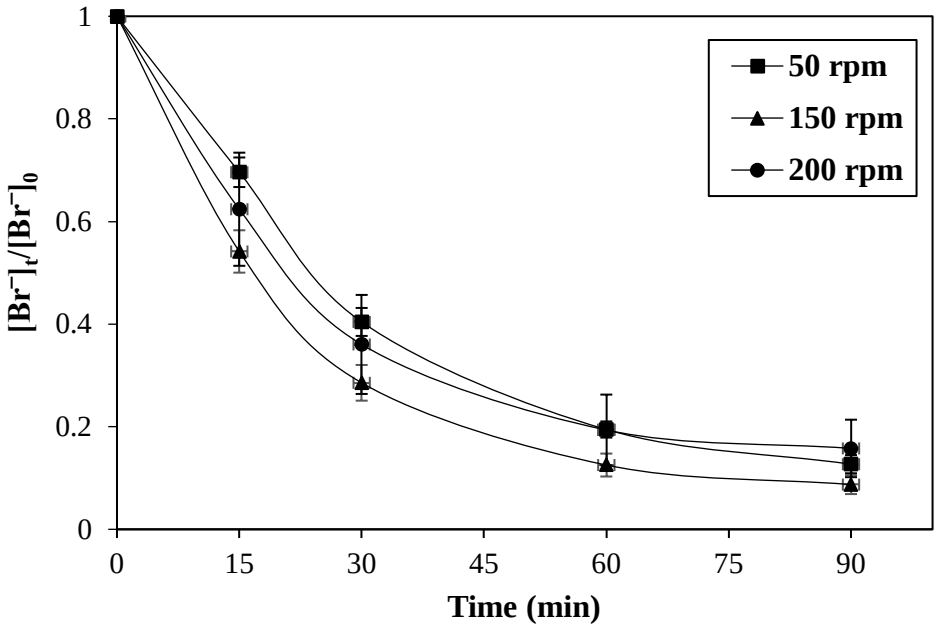


Figure 4-2: Bromide removal behaviour of pristine SIAC (400 mg) at different agitation speeds. Initial bromide concentration: 1mg/L (12.5 µM).

4.4.2 Bromide Uptake: Complexation with Silver vs Physisorption

Bromide solutions were stirred with a fixed amount of SIAC (0.4 g) for up to 3 hours. The bromide removals achieved were 98% and 93%, for the two lowest bromide concentrations of 12.5 and 25 µM, respectively (Figure 4-3a). As expected, the percent bromide removal decreased with increasing bromide concentration presumably due to the limited number of accessible silver sites to precipitate the bromide ions. These

trends are in agreement with similar studies reported elsewhere using various types of SIAC and also Ag-doped carbon aerogels (Chen et al. 2017; Sánchez-Polo et al. 2007).

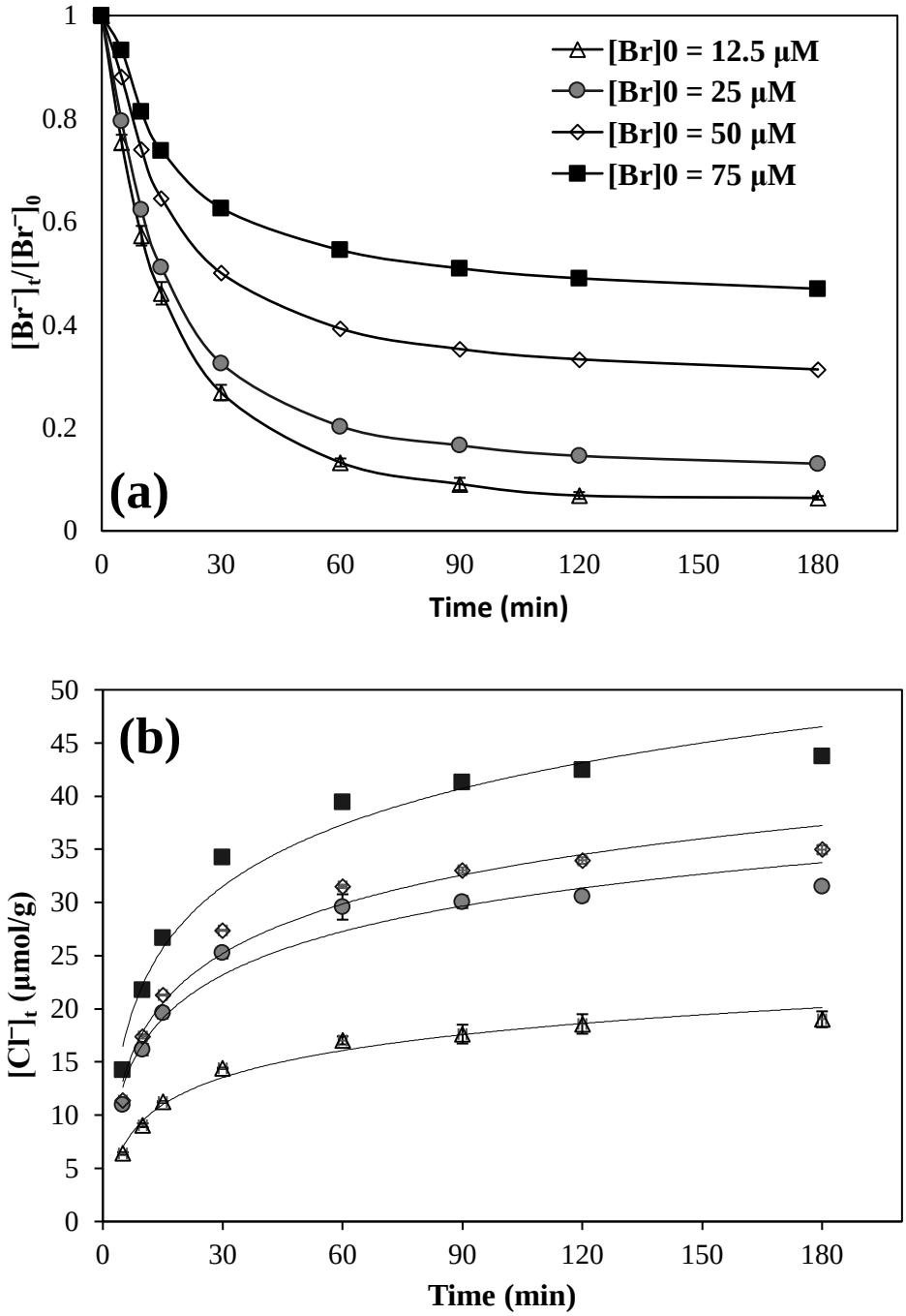


Figure 4-3: (a) Bromide uptake and (b) chloride release from unconditioned SIAC (400 mg). Initial bromide concentrations: 2.5, 25, 50 and75 µM.

However, the amount of bromide removed by the SIAC (up to 50 µM) was significantly higher than the silver content of SIAC (13.6 µmol/g equal to 0.11 wt% reported by the manufacturer). Therefore, these results suggest that there may be other

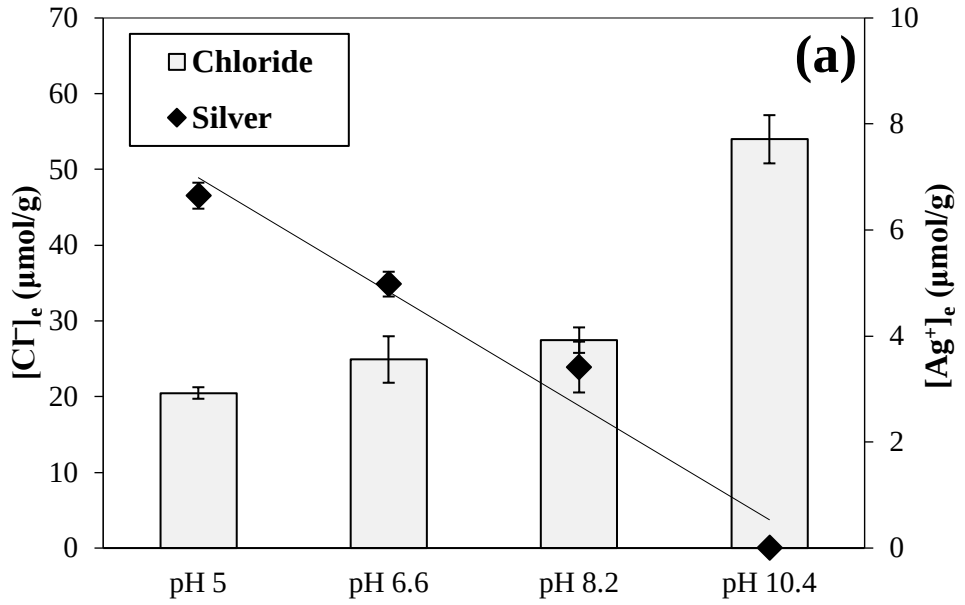
mechanisms involved in the bromide removal by SIAC, since there is not enough silver to react with all the bromide. As in Figure 2a, the bromide concentration was significantly reduced from 25 µM to less than 1 µM indicating a 93% bromide removal efficiency. However, when the initial bromide concentration was increased to 75 µM, only 53% of bromide was removed through SIAC. The uptake of bromide was inversely correlated with the release of chloride into solution, with increasing initial bromide concentrations promoting greater release of chloride to the solution (Figure 4-3b), suggesting the involvement of an ion exchange process (i.e. bromide ions exchange with chloride ions entrained within the SIAC pores). For example at 75 µM intial bromide concentration, almost 40 and 43.7 µM of bromide removal and chloride residual were achieved, respectively. In a blank experiment without bromide, the extent of silver and chloride leaching were determined over the first 90 minutes of contact time, where pH decreased from 6.5 to 4.3 (Figure 4-1 at 150 rpm). The pH decrease was probably due to increased dissolution of carbon dioxide in the unbuffered blank solution. The amount of silver leached into the solution was similar to that of chloride (with a maximum of 6.5 µmol/g). This suggests that most of the silver may be leached out from pristine SIAC as AgCl. A maximum of less than 1 µmol/g of nitrate was leached from SIAC for a contact time of 180 min, suggesting that in our conditions the silver leaching from SIAC was not in the form of silver nitrate as had been suggested in a previous study (Watson et al. 2016).

The point of zero charge pH (pH_{PZC}) has been used to determine the electrostatic properties of SIAC and Ag-doped aerogels in bromide removal applications (Chen et al. 2017; Sánchez-Polo et al. 2007). The SIAC pH_{PZC} was measured as 7.2 which was greater than the solution pH (6.5) and therefore, the SIAC surface would be positively charged ($pH_{solution} < pH_{PZC}$). Consequently, the attraction of bromide anions to the SIAC by electrostatic interactions would be favoured. Since AgBr is less soluble than AgCl, the formation of AgBr (s) is favoured over the formation of AgCl(s) during the bromide removal process. Apart from silver-halide interactions, the bromide removal pathway via electrostatic interaction with SIAC (physisorption) would be unfavourable in natural waters, where the concentration of chloride is typically 300-fold greater than that of bromide (Sánchez-Polo et al. 2007; Watson et al. 2016). In addition, silver leaching from conventional SIAC is significant. Both of these considerations limit the practicality of using conventional SIAC in drinking water

treatment operations. Therefore, novel approaches to mitigate silver leaching and also to limit the bromide removal pathway to direct complexation with silver on the surface of SIAC were investigated.

4.4.3 Preconditioning of SIAC for Improved Performance: Mitigation of Silver Leaching

In order to identify the capacity of SIAC for the removal of bromide via direct complexation with silver, the SIAC was washed at various pH values and ionic strengths in order to remove part of the chloride. The extent of silver and chloride leaching after three hours in solutions containing 400 mg of SIAC is shown in Figure 4-4a and b. The amount of chloride leaching increased with increasing pH from 6.6 to 10.4 for pristine SIAC, where the amount of chloride released from the SIAC reached its maximum at pH 10.4 (Figure 4-4a). This is suggestive of displacement of Cl^- by hydroxide (OH^-) from the SIAC surface. In another experiment, the influence of ionic strength was investigated. Sodium perchlorate was used because the perchlorate ion is less likely than other ions to precipitate silver and has a high affinity to replace the chloride on the surface of the SIAC (Gu et al. 2001; Haynes 2014).



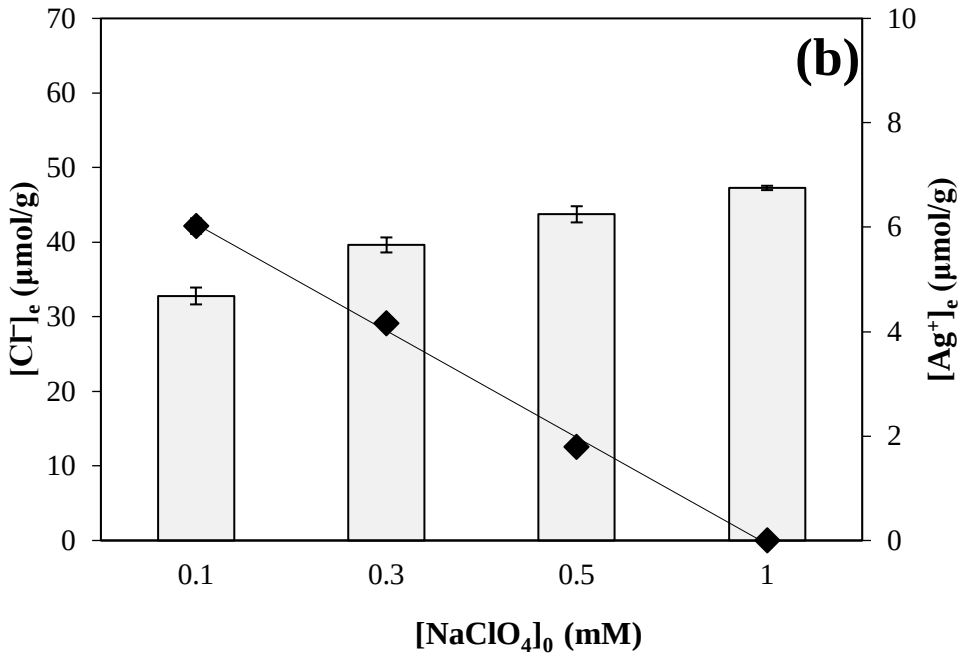


Figure 4-4: (a) Effect of increasing the pH of the SIAC treatment solution on the amount of silver and chloride leaching from the SIACand (b) effect of increasing ionic strength at fixed initial pH (8.2) on the amount of silver and chloride leaching from the SIAC.

Increasing sodium perchlorate concentration slightly increased chloride release and significantly reduced silver leaching (Figure 4-4b). From these results, two methods for preconditioning the SIAC were selected: (a) pH 8.2 with $NaClO_4$ at 1 mM and (b) pH 10.4 without $NaClO_4$. The preconditioning procedures were repeated five times using fresh solutions at each stage to maximise chloride removal from SIAC. In both cases the highest levels of both silver and chloride were leached in the first step (Tables 4-1). However, the higher affinity of hydroxide groups for the exchange with chloride compared to that of perchlorate led to higher chloride leaching when SIAC was treated at pH 10.4 compared to 1 mM $NaClO_4$ at pH 8.2.

Table 4-1: Silver and chloride leaching from the SIAC during preconditioning (at pH 10.4 and in 1mM of $NaClO_4$ at pH 8.2). Samples were filtered through 0.22µm filter membrane prior to analysis.

Number of Treatments	**$[Ag^+]$ (µmol/g)**	**$[Cl^-]$ (µmol/g)**	**$pH_{t=30min}$**
1^{st}treatment (pH 8.2, 1mM $NaClO_4$)	0.06	13.8 ± 0.1	7.7
2^{nd}treatment (pH 8.2, 1mM $NaClO_4$)	0.04	8.3 ± 0.2	7.6
3^{rd}treatment (pH 8.2, 1mM $NaClO_4$)	0.03	7.0 ± 0.4	7.5
4^{th}treatment (pH 8.2, 1mM $NaClO_4$)	0.06	5.6 ± 0.2	7.8
5^{th}treatment (pH 8.2, 1mM $NaClO_4$)	0.05	6.6 ± 0.1	8.0
1^{st}treatment (pH 10.4)	0.15	31.4 ± 0.37	9.2
2^{nd}treatment (pH 10.4)	0.05	21.0 ± 2.42	9.6
3^{rd}treatment (pH 10.4)	0.08	7.4 ± 0.04	9.9
4^{th}treatment (pH 10.4)	< LOD	3.1 ± 0.05	10.1
5^{th} treatment (pH 10.4)	< LOD	2.0 ± 0.1	10.1

To further confirm these impacts, the rate of silver and chloride leaching from the SIAC treated under each preconditioning environment were examined by measuring the appearance of Ag^+ and Cl^- in ultrapure water (Figures 4-5a and b). Comparing the silver leaching results for preconditioned SIAC (Figure 4-5a) with those of pristine SIAC (Figure 4-1) clearly showed that both preconditioning methods were successful in minimising silver leaching. However, in the SIAC preconditioned at pH 10.4, silver concentrations in the solution were below the analytical detection limit (0.02 mg/L) during the 180 min of the experiment, compared to 5.3 µmol/g after 90 minutes from pristine SIAC (Figure 4-1). Additionally, the amount of chloride released from the SIAC preconditioned in perchlorate solution at pH 8.2 (Figure 4-5a) was similar to that released from pristine SIAC (Figure 4-1), whereas preconditioning at pH 10.4 significantly decreased the leaching of chloride (Figure 4-5b). These results indicated that preconditioning at pH 10.4 may be more beneficial than preconditioning using 1 mM $NaClO_4$ at pH 8.2.

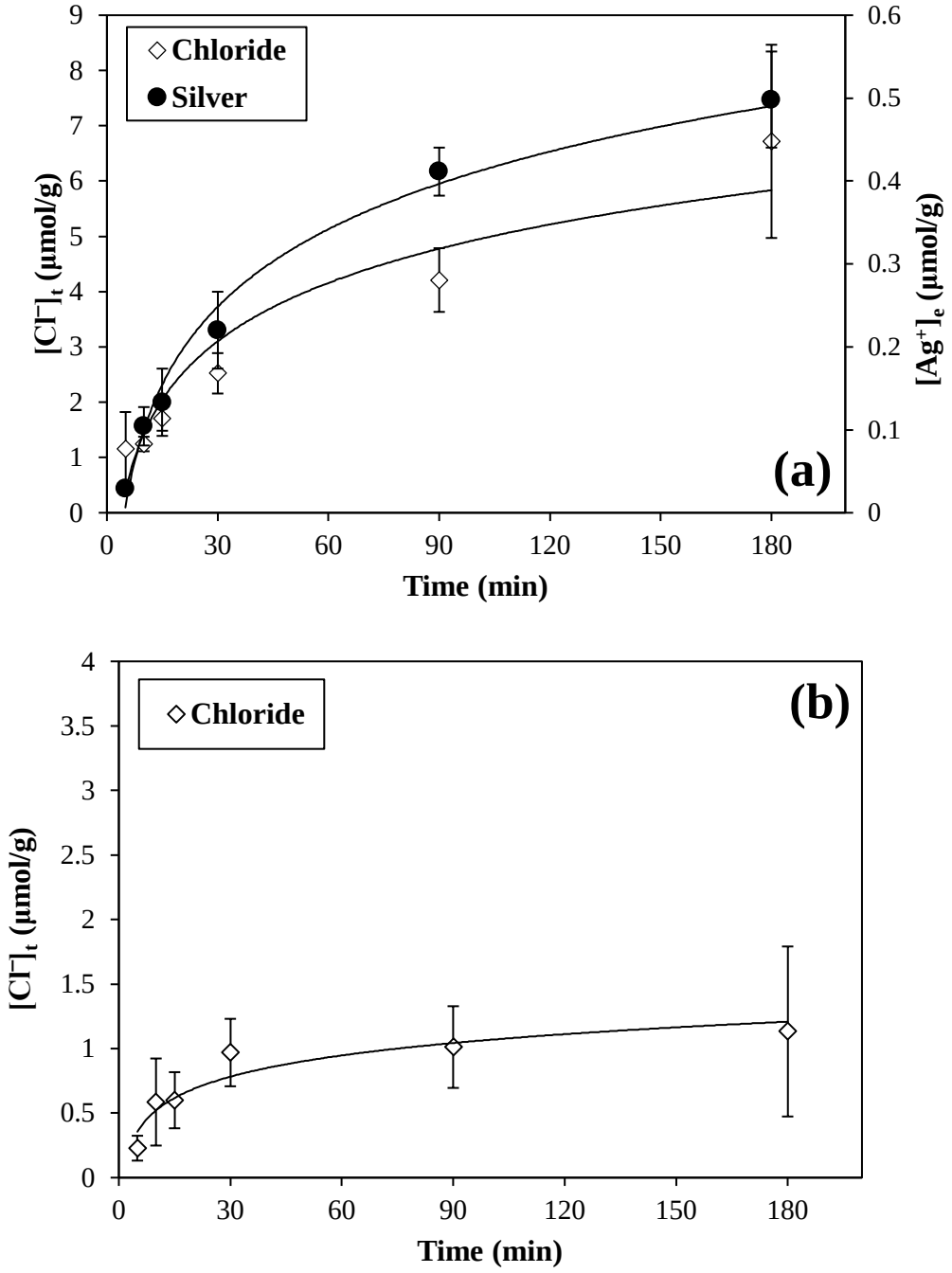


Figure 4-5: Effect of preconditioning on ion release behaviour: 1 mM of $NaClO_4$ (a) at pH 8.2 and (b) at pH 10.4. Mass of preconditioned SIAC: 400 mg. Silver was below the limit of detection (0.02 mg/L) in (b).

To further assess the efficiency of various preconditioning approaches, the mass of silver coating was determined before and after bromide removal experiments using different types of SIAC. Previous studies on silver leaching have shown that iodide removal from solution using SIAC could occur either via the immobilisation of iodide on silver ion attached to the SIAC or by precipitation of silver ion in solution to form

suspended silver precipitates (Hoskins et al. 2002). The concentrations of dissolved and immobilised silver in solution were followed before and after bromide removal experiments using both pristine and conditioned SIAC. Batch experiments were performed in which SIAC was stirred in the presence of 12.5 µM initial bromide for 3 hours in ultrapure water with no interfering ions. The total amount of silver in solution was determined by direct acidification of the solution after removing the SIAC granules by filtering the final solutions through grade 4 qualitative filter paper. Preconditioning at pH 10.4 showed the highest amount of silver retained on the SIAC, with minimal difference (less than 3%) between the initial (13.2 µmol/g) and final (12.9 µmol/g) silver on the SIAC being observed (Table 4-2).

Table 4-2: Silver mass balance for pristine and preconditioned SIAC. Initial bromide concentration: 12.5 µM. Contact time: 3 h. Mixing speed: 150 rpm. SIAC dose: 0.8 g/L. Initial pH 6.5.

	No further treatment (µmol/g)	**Treated at pH 8.2, 1mM $NaClO_4$ (µmol/g)**	**Treated at pH 10.4 (µmol/g)**
$[Ag^+]_{t=0}$Initial silver coating on the SIAC after preconditioning	13.6 ± 0.8	9.1 ± 0.3	13.2 ± 0.5
$[Ag^+]_{t=180min}$ Dissolved in solution	1.3± 0.1	0.5± 0.1	< LOD
$[Ag^+]_{t=180min}$ Total (precipitated + dissolved) in solution	3.8 ± 0.1	1.7 ± 0.1	0.8 ± 0.1
$[Ag^+]_{t=180min}$ Remaining on the SIAC	8.1 ± 0.2	7.6 ± 0.3	12.9 ± 0.1
Silver loss (%)	40	16.5	3

Preconditioning in 1 mM of perchlorate solution at pH 8.2 still significantly reduced the silver loss compared to pristine SIAC (40% loss using pristine SIAC compared to about 16% loss using the preconditioned SIAC). Therefore, the highest silver residual was achieved for the SIAC conditioned at pH 10.4, likely representing silver bromide (or chloride) precipitates trapped into the carbon substrate. On the other hand, SIAC with no preconditioning had the highest silver loss after 3 hours (Table 4-2).

A schematic illustrating the proposed interactions between the silver particles with halide is shown in Figure 4-6. When $pH_{solution}<pH_{PZC}$, the SIAC is in a favourable condition to hold Ag^+ which attracts the negatively charged halides from the solution

via chemisorption (pathway 1). When $pH_{solution} > pH_{PZC}$, silver is released from the SIAC to the bulk solution and repulsive electrostatic interactions between negatively charged SIAC and halides occur, leading to the formation of AgX in the aqueous phase (pathway 2).

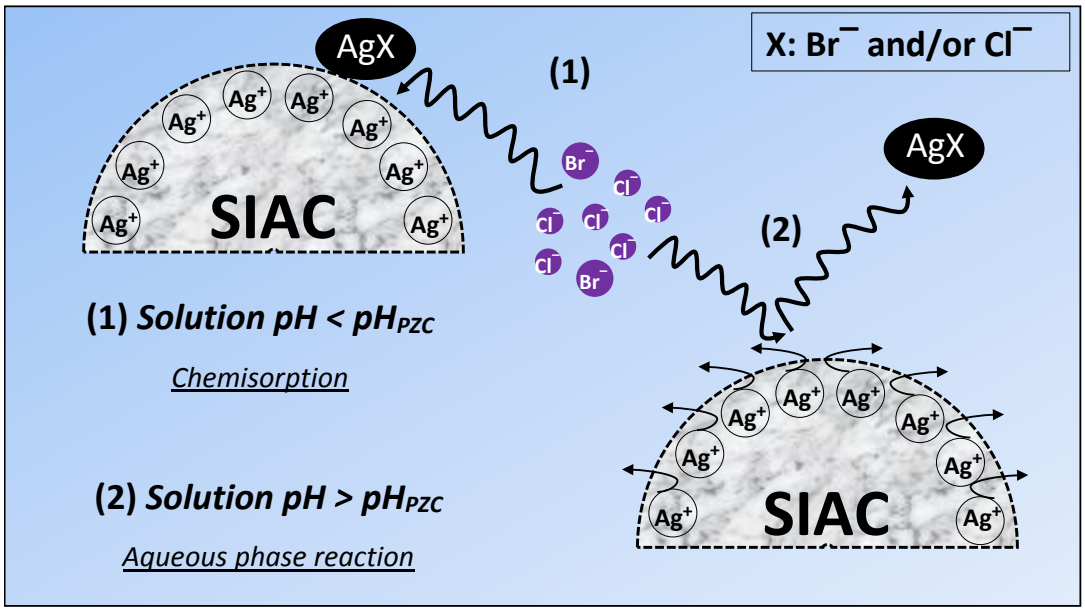
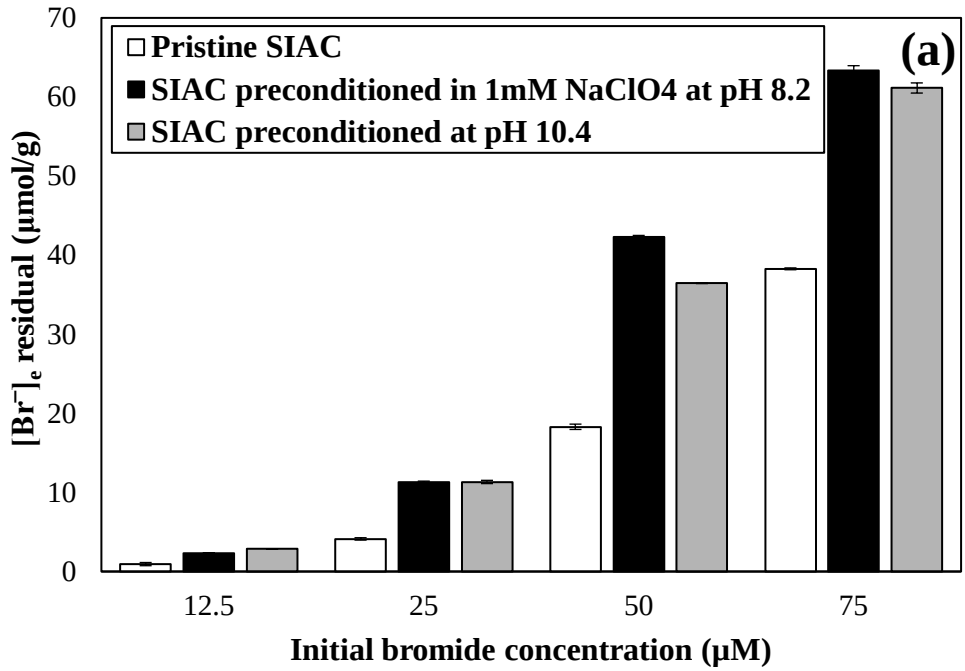


Figure 4-6: Schematic illustration of the proposed interactions of pristine SIAC with silver ions as a function of solution pH.

In this study, both pristine and preconditioned SIAC are expected to be positively charged in solution (pathway 1). However, it is hypothesised that the chloride contamination of the pristine SIAC leads to a release of silver to the solution. The higher AgCl solubility allows it to diffuse into the bulk solution, as opposed to immediate precipitation on the Ag coating and thereby causes a high loss of Ag. On the other hand, the AgBr solubility is extremely low ($K_{sp} = 5.2 \times 10^{-13}$)(Haynes 2014), therefore, any AgBr formed will tend to precipitate immediately on the adjacent Ag coating in the process of surface co-precipitation (Stumm 1992). Overall, the preconditioning of SIAC at high pH has high potential to alter the bromide and silver interaction from an unwanted aqueous phase precipitation reaction to a desirable chemisorption mechanism (i.e. surface co-precipitation) occurring on the surface of the SIAC.

4.4.4 Performance Evaluation of Preconditioned SIAC

In order to further assess the impact of the preconditioning processes in minimising silver leaching from the SIAC at higher bromide concentrations, the concentrations of bromide and chloride were measured for both the pristine and the preconditioned SIAC samples (Figure 4-7a and b). The use of pristine SIAC resulted in a higher bromide uptake from the solution compared to the preconditioned SIAC samples. However, the amount of silver incorporation (Table 4-2) was significantly lower than the amount of bromide removed by pristine SIAC which indicates that a large proportion of the bromide was removed through attractive electrostatic (physisorption) interactions, rather than silver-bromide reactions. This removal mechanism would not be practical in a real water matrix where the chloride ions are present in much higher amounts than bromide (Br^-/Cl^- ratio of 1:300 by weight) because the extent of physisorption for chloride would be similar to that for bromide, i.e., there is less preferential removal of bromide in the physisorption mechanism than in the silver halide formation mechanism. Furthermore, due to the negative surface charge of pristine SIAC in natural water systems (pH ≥ 7), the propensity for adsorption of bromide to the surface of SIAC would be weaker.



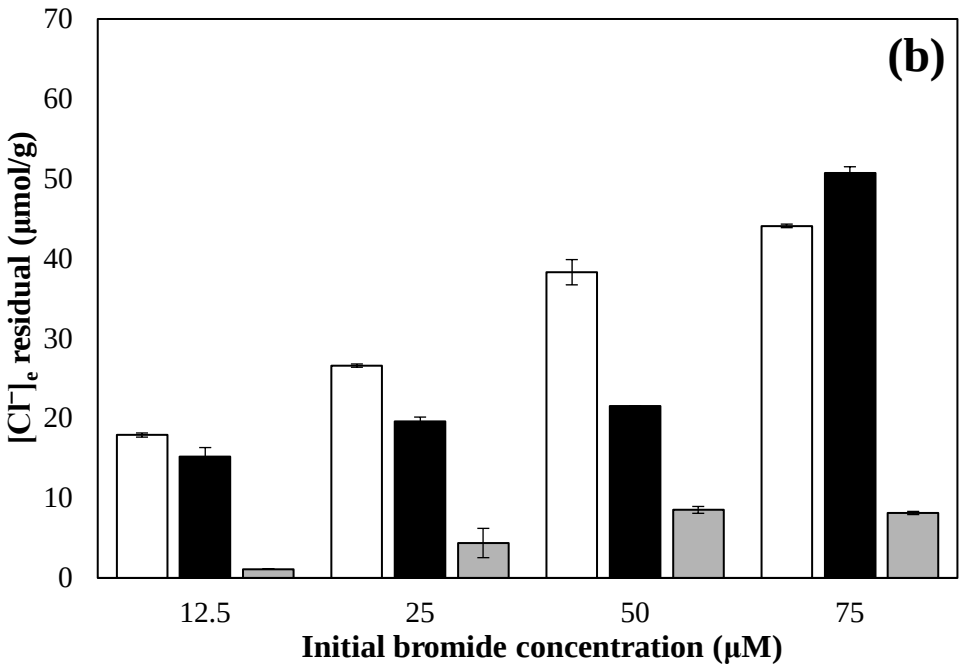


Figure 4-7: Effect of preconditioning on (a) bromide and (b) chloride residuals in solution. Batch experiment of three hours; initial bromide concentrations: 12.5, 25, 50 and 75 µM; SIAC mass: 400 mg.

To find out to what extent the reaction between silver and bromide occurred on the surface of SIAC, the concentration of silver remaining on the SIAC was quantified after the bromide removal experiment (Figure 4-8). As a general trend, the higher the concentration of bromide the lower the silver residual and, therefore, it was concluded that exposure to higher bromide concentrations resulted in higher amounts of silver being released into solution. However, the extent of silver release for the SIAC preconditioned at pH 10.4 was much lower than the SIAC preconditioned at pH 8.2 and the pristine SIAC. These results further demonstrate the effectiveness of SIAC preconditioning at high pH to minimise silver loss.

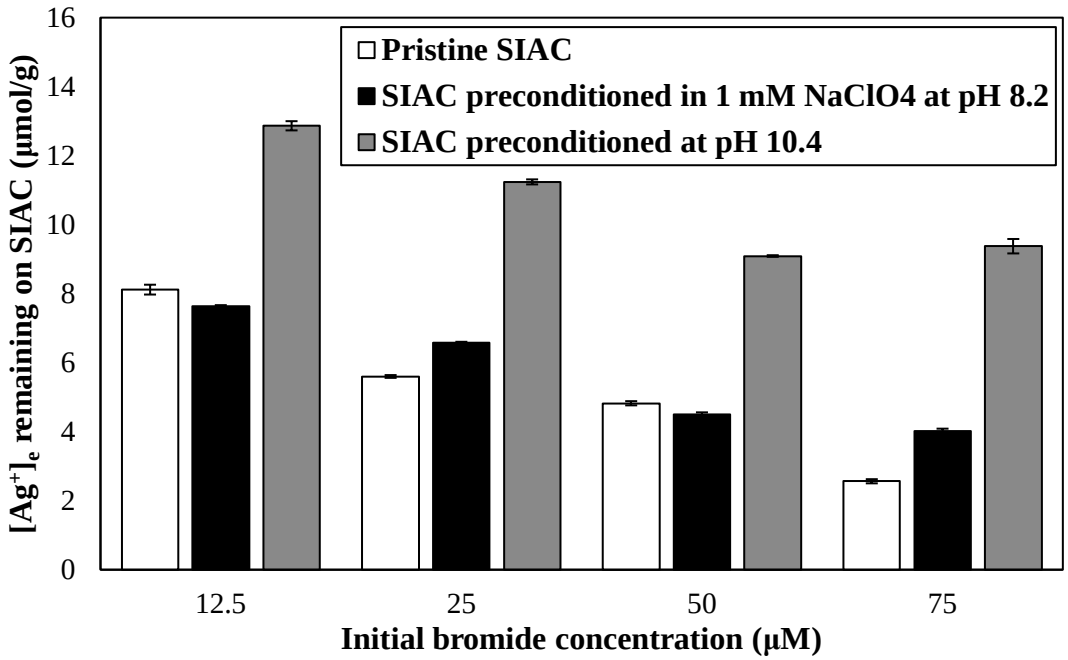


Figure 4-8: Effect of preconditioning and bromide initial concentration on the total concentration of silver remaining on SIAC. Contact time: 3 hours; mass of SIAC: 400 mg.

Given that SIAC preconditioned at high pH was the most promising in terms of minimal silver leaching, the SIAC particles subjected to this treatment were further investigated in a more complex environment. Figure 4-9 shows the extent of silver leaching and bromide removal of both the pristine SIAC and the SIAC preconditioned at pH 10.4 in the presence of dissolved chloride and in a real water sample. For all types of SIAC, it was found that increasing the concentration of chloride and bromide increased the AgX precipitation reaction, resulting in increased concentrations of total silver residuals in solution. The silver leaching results were also compared to those obtained in a real groundwater matrix, where the concentrations of bromide and chloride were 22.5 µM and 16 mM (1.8 and 57 mg/L), respectively. The bromide residual results obtained for both types of SIAC revealed a similar bromide removal capacity in synthetic and real water samples, revealing that the preconditioning did not deteriorate the SIAC efficiency for the bromide removal application. For a fixed amount of SIAC, the higher concentration of chloride resulted in a higher bromide residual left in the solution, due to the limitation of available silver sites on the SIAC. However, SIAC preconditioned at pH 10.4 had significantly lower silver leaching in the real water sample compared to pristine SIAC. As expected with a real water sample (pH 8.6), both pristine (pH_{PZC}=7.2) and preconditioned (pH_{PZC}=8.1) SIAC would be

negatively charged ($pH_{solution}>pH_{PZC}$) so that the repulsive electrostatic interactions between the SIAC surface and halides could generate an aqueous-phase reaction between silver and bromide. As a result, the amount of silver leaching in preconditioned SIAC has slightly increased compared to the extent of silver leaching obtained for synthetic water samples at pH 6.5.

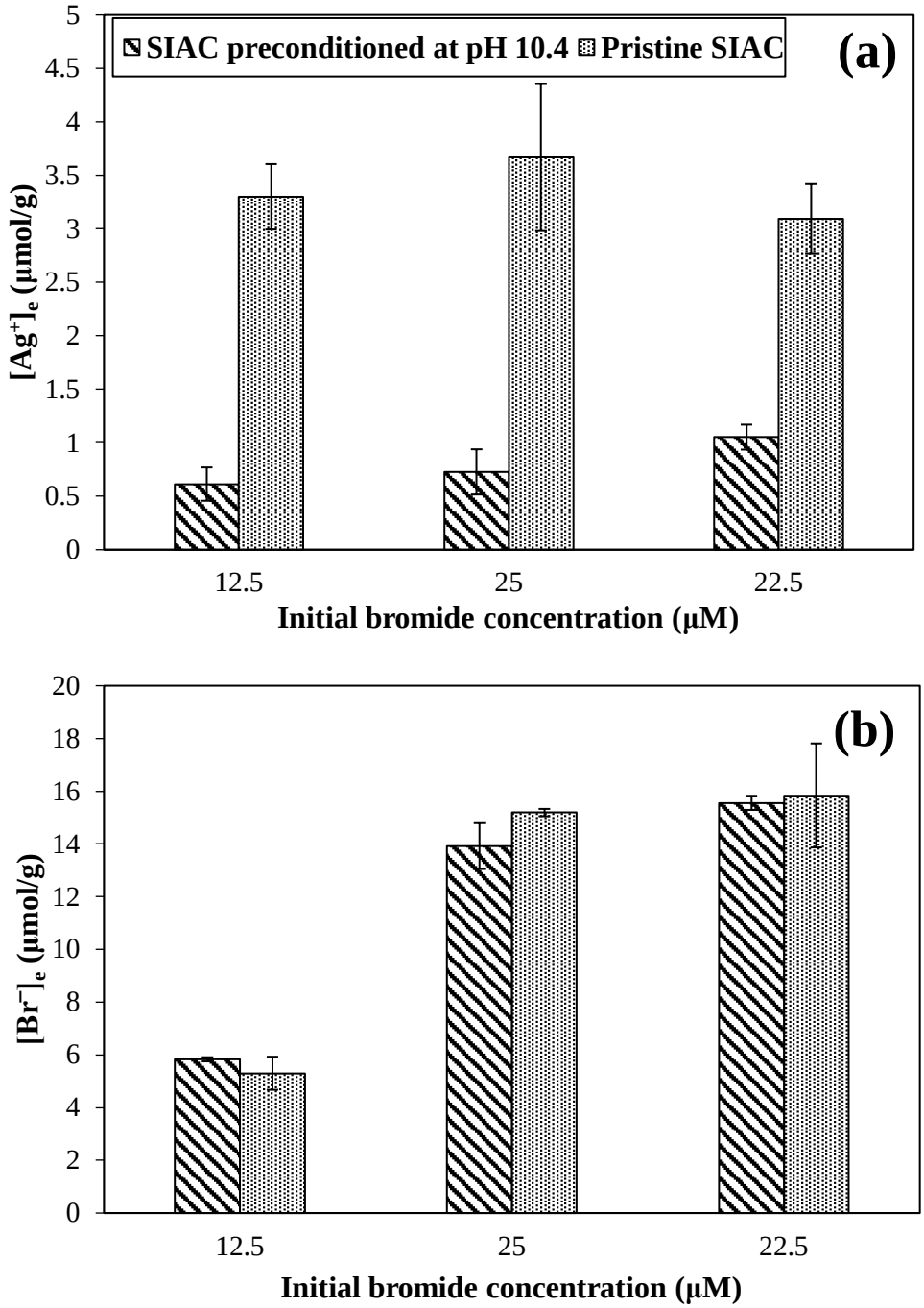


Figure 4-9: (a) Silver and (b) bromide residuals in solution after treatment of real or synthetic waters with pristine or preconditioned SIAC (400 mg) in the presence of

excess chloride. Br^-/Cl^- ratio of 1:300 by weight in synthetic water and 1:350 by weight in real water sample. Contact time: 3 hours.

In terms of NOM removal, both types of SIAC had similar initial NOM removal capacities but the pristine SIAC had better removal over longer contact times (24 and 72 hours: Figure 4-10). At pH 8.6 where the surfaces of both the pristine and the preconditioned SIAC are negatively charged, there is an electrostatic repulsion between the negatively charged NOM molecules and the SIAC surfaces.

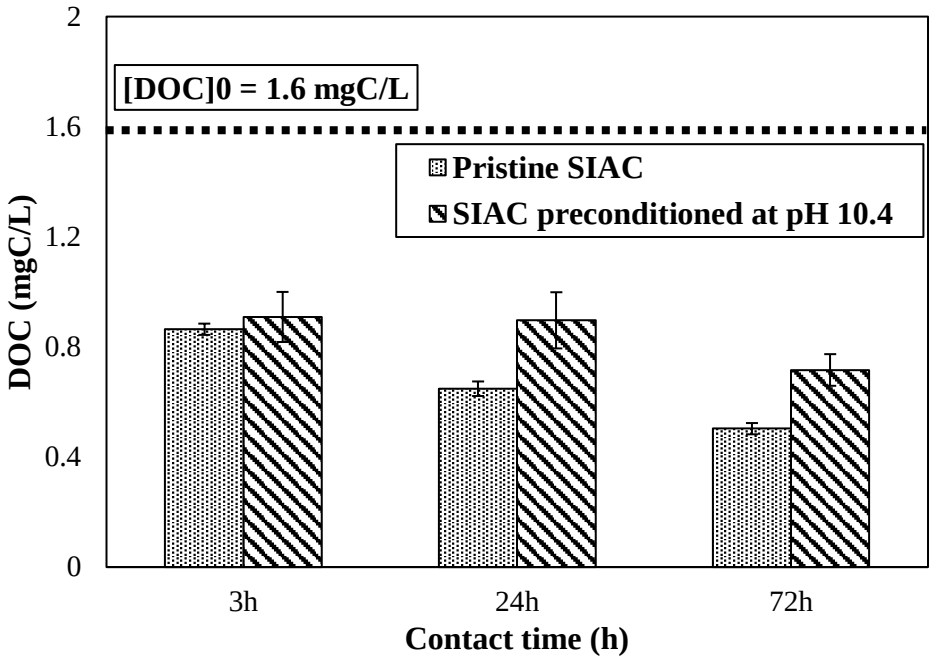


Figure 4-10: DOC uptake in real water by pristine or preconditioned SIAC. Initial DOC concentration: 1.6 mgC/L.

Therefore, the non-electrostatic adsorption of organic matter can be attributed to two mechanisms: through the weak dispersion forces between the SIAC surface and less polar (humic) sites of NOM molecules and through hydrogen bonding between the hydrogen atoms on the SIAC surface and polar (non-humic) sites of NOM molecules (Newcombe 1999).

4.5 Conclusions

In this study, the impact of SIAC preconditioning on the bromide removal capacity and minimisation of silver leaching from a commercially available SIAC was investigated. Unlike previous research where the silver leaching properties of SIAC were not studied in detail, our study focused on several factors determining the

practicalities of the use of SIAC for bromide removal, including the kinetics of bromide adsorption and, in particular, the leaching of silver from the SIAC into the treated water. It was found that preconditioning at pH above 10 decreased the release of Ag^+ and immobilised silver halides by 40% and did not deteriorate the capacity of SIAC to remove bromide. Also, preconditioning in 1 mM of perchlorate solution at pH 8.2 significantly reduced the silver loss from 40% to about 16%. Comparing the initial silver coatings between both types of preconditioned SIAC revealed that SIAC treatment at high pH (10.4) was more beneficial to minimise loss of silver, while preconditioning in 1 mM perchlorate solution at pH 8.2did not lead to a significant reduction in silver leaching. Overall, the study indicated that the preconditioning of SIAC at high pH has good potential to alter the bromide and silver interaction from an unwanted aqueous phase precipitation reaction to a desirable chemisorption mechanism occurring on the surface of the SIAC. To achieve a better understanding of the practical implication of preconditioning on this type of SIAC, a natural water matrix was tested using both pristine SIAC and SIAC preconditioned at pH 10.4. Silver leaching and bromide removal using both pristine and preconditioned SIAC at pH 10.4 in the presence of dissolved chloride (Br^-/Cl^- ratio of 1:300 by weight) and in a real water sample were determined. Our results revealed that the preconditioning greatly decreased the release of Ag in solution for real waters. Also chloride has the most interfering role, reducing the bromide removal efficiency as well as increasing the extent of silver leaching from the SIAC during the first three hours. Both pristine and preconditioned SIAC removed NOM as well as bromide, but the pristine SIAC had a slightly higher NOM removal capacity after contact times greater than 24 hours.

Chapter 5

The Effect of Natural Organic Matter on Bromide Removal Using Silver-impregnated Activated Carbon

5.1 Abstract

In this chapter, a further investigation into the impact of natural organic matter (NOM) on the bromide (Br^-) removal capacity of silver-impregnated activated carbon was conducted. For this purpose, a commercially available SIAC was used to evaluate the impact of various NOM extracts with different physiochemical characteristics ($2.51 \leq SUVA_{254} \leq 5.16$) on the extent of Br^- removal. Similarly for all types of NOM extracts, increasing the SIAC dosage from 0.5 to 2 g/L significantly improved both the bromide and NOM removal, most likely due to the increase of available active sites on the SIAC that react with both bromide and NOM molecules. All types of NOM extracts were shown to reduce bromide removal through SIAC, but a distinguishable difference in bromide removal was observed for the different NOM extracts. It was found that the chemical composition of NOM affected the extent of bromide removal, where sulphur–rich NOM more significantly decreased bromide removal efficiency so that the NOM removal is improved (i.e. NOM removal appeared to occur at the expense of bromide removal). Additionally, the coexistence of nitrogen-rich NOM with high affinity towards Ag^+ sites on SIAC resulted in the highest extent of silver leaching into solution. The findings obtained from NOM extracts were further supported by studies using small model compounds including glycine (nitrogen-rich), thioglycolic acid (sulphur–rich) and sodium propionate (control). The sulphur–containing (thiol) organic model compound thioglycolic acid lowered the bromide removal efficiency from above 95 to 60%, which corresponded to the inactivation of SIAC adsorption sites by direct complexation of Ag^+ with the thiol electron donating group. In contrast to the effect of thioglycolic acid, the coexistence of glycine did not significantly reduce the bromide removal capacity but the extent of silver leaching was increased due to the significantly lower solubility of silver bromide (5.2×10^{-13}) compared to that of silver-glycine (1.28×10^{-7}). Therefore, anion exchange of glycine for bromide is expected to occur. As a result, an alternative bromide removal pathway can be considered through glycine complexation of Ag^+ followed by the bromide-glycine anion exchange reaction. These observations suggest that in addition to the physical characteristics of NOM (molecular weight distribution), its chemical composition is also important in determining the extent of bromide removal and silver leaching of SIAC.

5.2 Introduction

Potentially carcinogenic halogenated disinfection by-products (DBPs) are largely sourced from two main water constituents: a) naturally occurring bromide and natural organic matter (NOM) (Richardson et al. 1999; Singer 1999; Chang et al. 2001; Criquet et al. 2012; Tan et al. 2016). Given that the reactivity and toxicity of Br-DBPs are about three orders of magnitude higher than their chlorinated analogues (Plewa et al. 2002), significant efforts are being made to develop water treatment processes to remove NOM or minimise its reactivity with bromide to form brominated DBPs (Br-DBPs). These processes include various oxidative pre-treatment strategies such as ozone (O_3) (Buffle et al. 2006; Chiang et al. 2009; Hua et al. 2013), permanganate (MnO_4^-)(Zhao et al. 2016), chlorine dioxide (ClO_2)(Yang et al. 2013) and ferrate (Fe(VI))(Goodwill et al. 2015; Jiang et al. 2015, 2016, 2016). While many treatment processes have been applied for effective removal of NOM (Karanfil et al. 1999; Vilgé-Ritter et al. 1999; Chellam 2000; Miaomiao Zhang et al. 2003; Boyer et al. 2008; Ding et al. 2008; Hyung et al. 2008; Ando et al. 2010), there is a limited number of methods for the selective removal of bromide from natural water sources (Watson et al. 2012). Among all of the treatments tested, silver-impregnated adsorbents have shown a versatile capacity for halide removal from aqueous solution and the consequent minimisation of formation of halogenated DBPs (Hoskins et al. 2002; Sánchez-Polo et al. 2007; Gong et al. 2013; Polo et al. 2016; Watson et al. 2016; Chen et al. 2017). Thus, while these materials are promising for the removal of bromide, little is known about the impact of aquatic NOM on their efficiency.

Depending on the chemistry of water samples and also the surface charge of silver-incorporated adsorbents, the removal of various NOM fractions have been reported. Sánchez et al. (2007) have deduced two possible pathways for the interactions between NOM molecules and synthesised silver-impregnated carbon aerogels (Ag-doped aerogels): 1) blockage of carbon pores by adsorption of NOM and 2) inactivation of silver sites by scavenging either the Ag^+ on the surface or dissolved in the solution (Sánchez-Polo et al. 2007). In another study, they analysed the behaviour of a silver-doped polymeric cloth (Ag-cloth) in removal of bromide from a synthetic water matrix containing 5 mg/L tannic acid, as a model for dissolved organic matter (DOM) (Polo et al. 2016). Their results indicated that Ag-cloth has a significantly higher capacity to remove tannic acid molecules (156 mg/g) than bromide ions (0.88 mg/g), confirming

that the presence of organic matter reduced the capacity of the Ag-cloth to remove bromide. Gong et al. (2013) synthesised silver-loaded porous carbon spheres (SLPCSs) and evaluated their performance in removing traces of bromide from organic solutions (humic acid) (Gong et al. 2013). After addition of humic acid (HA) (4 mg/L), it was observed that the bromide removal efficiency significantly decreased from 95 to 21%.

Watson et al. 2016 reported an excellent bromide removal by a commercially available silver impregnated activated carbon (SIAC) (Ag content = 0.1 (wt%)) in the presence of various concentrations of Suwannee river NOM isolate (1R101N)). The authors observed around 20% NOM removal by SIAC which was attributed to adsorption onto the activated carbon component and hydrophobic interactions: electrostatic interactions with the silver sites were thought to be negligible. However, given the high affinity of NOM molecules towards metallic (Ag^0) and dissolved silver (Ag^+) (Adegboyega et al. 2013; Dobias et al. 2013; Yang et al. 2014; Gunsolus et al. 2015), it is essential to have a better understanding of NOM characteristics on bromide removal efficiency of SIAC in aquatic environments.

Given that fulvic acids account for a greater proportion of dissolved organic matter than humic acids in natural water systems (McKnight et al. 1998), a series of NOM and fulvic acids containing various functional groups (Table 5-1) has been employed for this study: Suwannee River fulvic acid (SRFA), Suwannee River dissolved organic matter (SRDOM) and Pony Lake fulvic acid (PLFA). The bromide removal efficiency by a commercially available SIAC was examined in the presence of these NOM isolates. The effects of the chemical elemental composition of NOM as well as its aromaticity as shown by the $SUVA_{254}$ value, on the efficiency of SIAC in removal of bromide were also studied. Based on the adsorbability of NOM isolates with different functionalities, three organic model compounds were chosen to further investigate the competitive effects of NOM isolates on SIAC performance.

5.3 Materials and Methods

5.3.1 Chemicals, Reagents and Analytical Methods

Silver nitrate ($AgNO_3$ AR grade, ≥99.5%) was obtained from Rowe Scientific Pty Ltd. Sodium bromide (NaBr ReagentPlus®, ≥99%), potassium nitrate (KNO_3 ACS reagent, ≥99.0%), glycine ($C_2H_5NO_2$ reagent grade, 98%), thioglycolic acid ($C_2H_4O_2S$ ≥98%) and sodium propionate ($C_3H_5NaO_2$ ≥99.0%) were all purchased from Sigma-Aldrich. All other reagents used including sodium chloride (NaCl), sodium hydroxide (NaOH), nitric acid (HNO_3, 70%) and hydrochloric acid (HCl, 34%) were supplied by Ajax Finechem Pty Ltd. These were of analytical reagent (AR) grade purity and were used without further purification. Ultrapure water produced by an ELGA water purification system (resistivity of 18.2 MΩ.cm) was used throughout this study for the preparation of reagents and solutions unless otherwise indicated.

Norit AG grade silver impregnated, granular activated carbon with 18×40 mesh size (0.42-1.00 mm) and nominal silver content of 0.1wt% and total surface area (S_{BET}) equal to 1050 m^2/g was provided by Cabot Norit, Amersfoort, The Netherlands. FILTRASORB® 400 granular activated carbon (F400) with effective size of 0.55–0.75 mm with no silver content was provided by Calgon Carbon Corporation, Pittsburgh, PA. The total silver concentrations in solutions were measured using a Varian Model SpectrAA 50 flame atomic absorption spectrophotometer (AAS) with a limit of detection (LOD) of 0.02 mg/L of Ag^+. Operating conditions for silver analysis were as follows: air/acetylene flame with a flowrate of 1.5/3.5 L/min, spectral slit width 0.5 nm, lamp current 4 mA and a wavelength of 328.1 nm were used throughout this study. The standard solutions were acquired via dilution of a stock solution of Ag^+ (1000 mg/L) prepared in HNO_3 (5% v/v) using ultrapure water**.** Bromide concentration was measured in a single method using a Dionex ICS-90 ion chromatography system with a Dionex IonPac AS9-SC (4.0 mm × 250 mm) analytical column.

Suwannee River fulvic acid (SRFA), Suwannee River dissolved organic matter (SRDOM) and Pony Lake fulvic acid (PLFA) were purchased from the International Humic Substances Society (IHSS). The details of the NOM samples are shown in Table 5-1. Each NOM stock solution (100 mgC/L) was prepared by dissolving the

NOM extract in ultrapure water, followed by filtration through 0.45 μm polyethersulfone syringe filters (Pall Life Science, Michigan, USA) and stored at 4 °C until extraction to prevent analyte degradation. NOM concentrations were measured using a total organic carbon (TOC) analyser connected to an auto-sampler (TOC-LCSH/CSN Model, Shimadzu Co., Kyoto, Japan). Calibration of the TOC instrument was carried out using potassium hydrogen phthalate standards (1–5 mg/L). The correlation coefficients of the calibrations were > 0.99 at all times. The ultraviolet absorbance at 254 nm (UV_{254}) of all samples was measured using a Cary 60 UV–Vis Spectrophotometer (Agilent Technologies, Australia) with a 1 cm quartz cell. The pH of the solution was measured using a Hach 40d pH meter equipped with PHC101 electrode.

5.3.2 Evaluation of Silver Concentration in Solution

In order to evaluate the dissolved and precipitated silver concentration in the working solutions, the SIAC was first removed from the solution by filtering the solution (500 mL) through grade 4 qualitative filter paper (pore size of 20~25 μm) followed by the addition of 6 mL concentrated HNO_3 . The solution was vigorously stirred and heated until the volume was reduced to about 50 mL. The final solution was made up to 100 mL with purified water in a volumetric flask prior to analysis using AAS.

5.3.3 Batch Adsorption Studies

Batch adsorption tests were carried out by adding dried SIAC samples (0.125, 0.25 and 0.5 g) at each run to synthetic water samples (250 mL). A jar testing apparatus with 6 stirring places equipped with a temperature-controlled water bath was used for the isothermal kinetic and equilibrium studies at 30 ± 0.5 °C with stirring speed of 150 rpm. In order to compare the ion uptake and leaching capacity of the SIAC for all experiments, the following correction factor was used:

$$C_e = \frac{V_L}{m_A}(C_{t,ins}) \qquad (5.1)$$

where C_e (mol/g) is the liquid-phase concentration per unit mass of SIAC, $C_{t,ins}$ is the liquid-phase concentration read in mol/L, V_L (L) is the total volume of solution and m_A (g) represents the mass of SIAC. No buffer solution was used for the purpose of

pH adjustment so that interference by coexisting ions could be prevented. The pH values were adjusted by addition of NaOH (10 mM) or HNO_3 (10 mM) and monitored during the experiments.

5.4 Results and Discussion

5.4.1 Reasons for Choosing NOM Extracts

Contradictory results of NOM inhibitory effects on bromide removal capacity of silver-impregnated materials have been reported in the literature. In studies on Ag-doped carbon aerogels Sánchez-Polo et al. 2007 observed a decrease in the bromide removal from surface waters containing 3.4 and 1.4 mgC/L of natural organic matter. This decrease in efficiency was attributed to blockage of pores within aerogels caused by the adsorption of the smaller NOM fractions (physisorption) as well as the direct complexation interaction of negatively charged NOM molecules with Ag^+ in the vicinity of the SIAC surface. Both mechanisms for the removal of NOM by silver-incorporated adsorbents is illustrated in Figure 5-1. Another group of researchers have reported a 21% increase in SRDOM (1R101N) removal using pristine Norit SIAC (0.1% Ag) while Br^- removal was greater than 90% across the sample matrix (Watson et al. 2016). The dominant mechanism for these observations was attributed to the adsorption of SRDOM onto the activated carbon component by hydrophobic interactions, while interactions with the silver sites appeared to be unimportant. These conflicting hypothesis were further investigated: the capacity of SIAC to remove bromide and NOM was evaluated in the presence of three NOM isolates, each with different chemical composition, spectral and molecular weight characteristics.

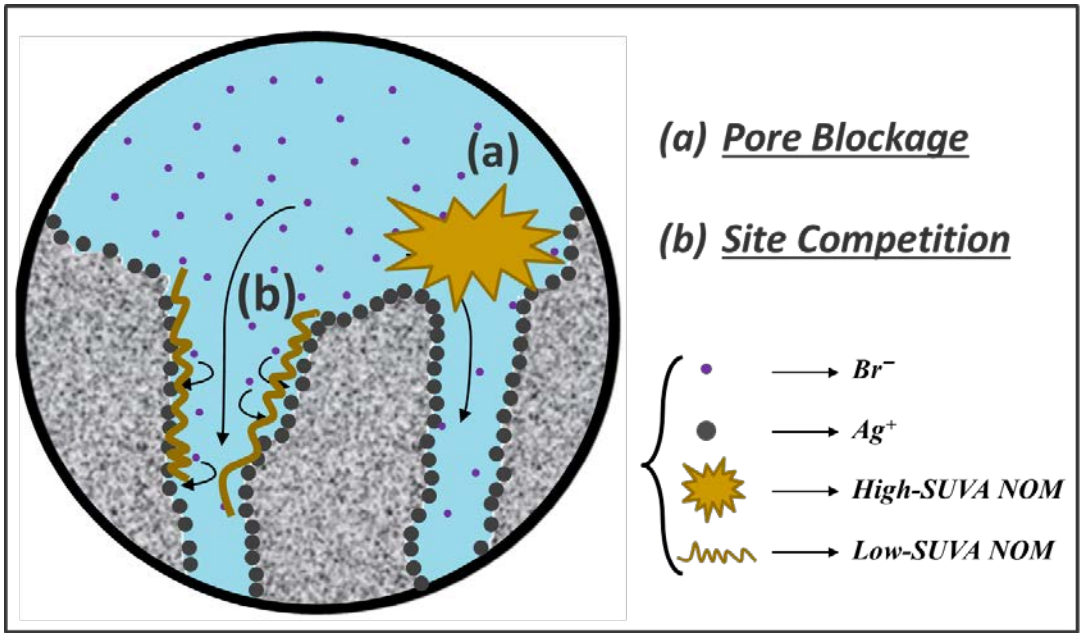


Figure 5-1: Schematic illustration of the proposed mechanisms for the interactions between SIAC and NOM

PLFA was chosen for this study due to its significantly higher sulphur and nitrogen content compared to those of SRFA and SRDOM (Table 5-1). Such electron donating groups have been reported to have a high affinity for Ag^+ and, therefore, a higher possibility of complexation reactions of Ag^+ (chemisorbed on the SIAC) is expected (Yang et al. 2014; Gunsolus et al. 2015). Furthermore, PLFA was reported as having a weight-averaged molecular weight between 1200 and 1400 Da which is the smallest compared to SRFA and SRDOM (Brown et al. 2004). Therefore, PLFA is expected to physically adsorb within the smaller pores of SIAC to a greater extent (Newcombe 1999). SRDOM, the next smallest NOM, has a higher nitrogen content compared to SRFA, but lower than that of PLFA and has quite a low sulphur content similar to the SRFA. SRDOM and SRFA have similar average molecular weights (Table5-1). The SRFA has the highest value of $SUVA_{254}$, which indicates that it contains a higher proportion of conjugated double bonds, including aromatic moieties. Some studies have reported that, due to its these electron-rich moieties, there would be strong non-electrostatic attractions between the aromatic rings of the SRFA molecules and hydrophobic sites of SIAC (Kilduff et al. 1996; Newcombe 1999).

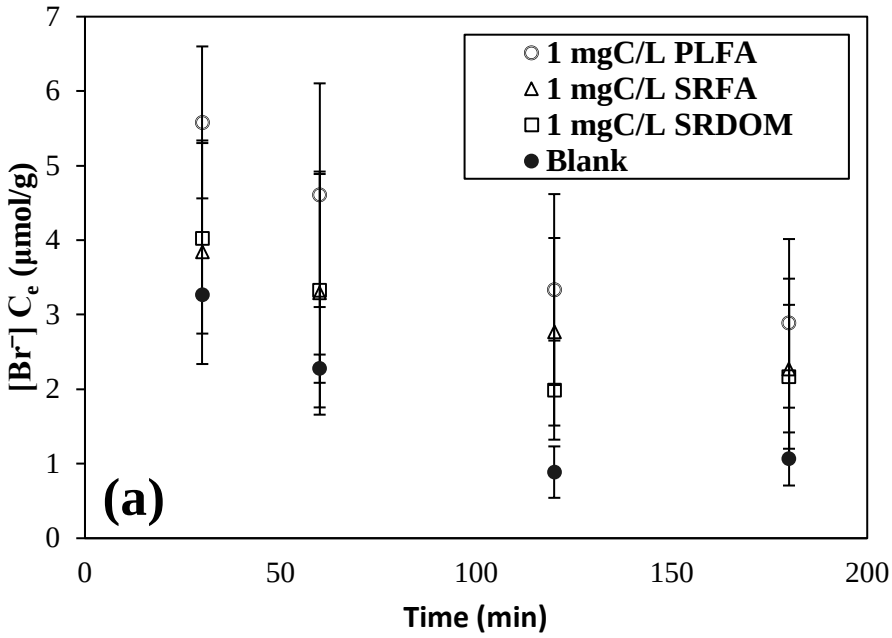
Table 5-1: Chemical properties of NOM isolates

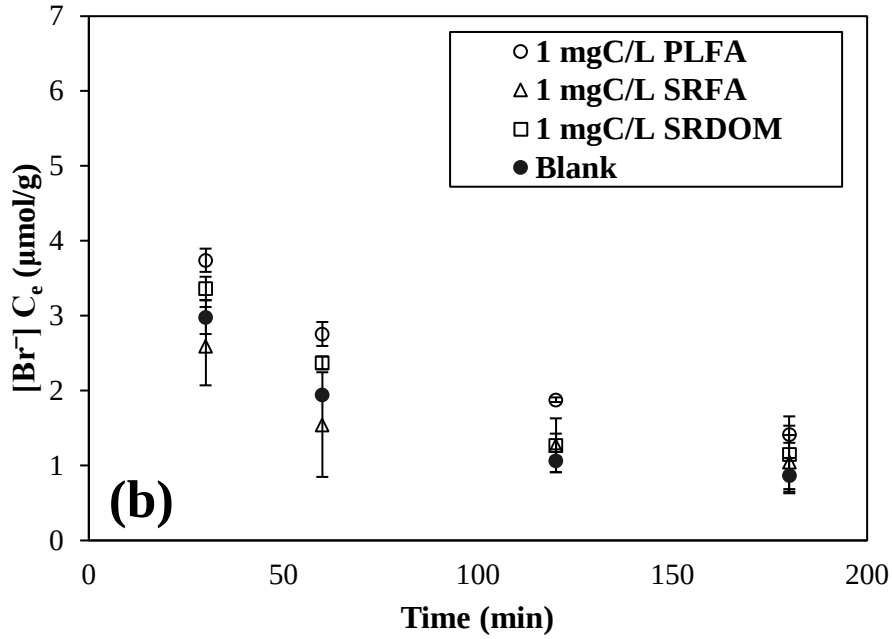
NOM isolate type	M_w[1]	$SUVA_{254}$	C[2]			O[2]	N[2]	S[2]
			(w/w)%	Aromatic (%)	Aliphatic (%)	(w/w)%	(w/w)%	(w/w)%
Pony Lake Fulvic Acid (PLFA) - 1R109F	1200 – 1400[3]	2.51	52.47	12	61	31.38	6.51	3.03
Suwannee River DOM (SRDOM) - 2R101N	2190[4]	3.84	50.70	24	33	41.48	1.27	1.78
Suwannee River Fulvic Acid (SRFA) - 2S101F	2310[4], 2290[5]	5.16	52.34	23	27	42.98	0.67	0.46

[1] *Weight averaged molecular weight (Louie et al. 2013)*
[2] *Elemental compositions of three NOM isolates obtained from the International Humic Substances Society (IHSS). The analyses were performed by Huffman Laboratories, Wheat Ridge, CO, USA; Isotopic analyses by Soil Biochemistry Laboratory, Dept. of Soil, Water, and Climate, University of Minnesota, St. Paul, MN, USA.*
[3] *Brown et al. (2004) (Brown et al. 2004)*
[4] *Chin et al. (1994) (Chin et al. 1994)*
[5] *O'Loughlin and Chin et al. (2004) (O'Loughlin et al. 2001)*

5.4.2 Impact of NOM on the Extent of Bromide Removal by SIAC

NOM was shown to decrease the capacity for bromide uptake by SIAC, with PLFA having the greatest effect on reduction of bromide removal and the effect being most pronounced at low SIAC doses. The effects of contact time and SIAC dosage were also determined to be important factors determining bromide removal (Figure 5-2).





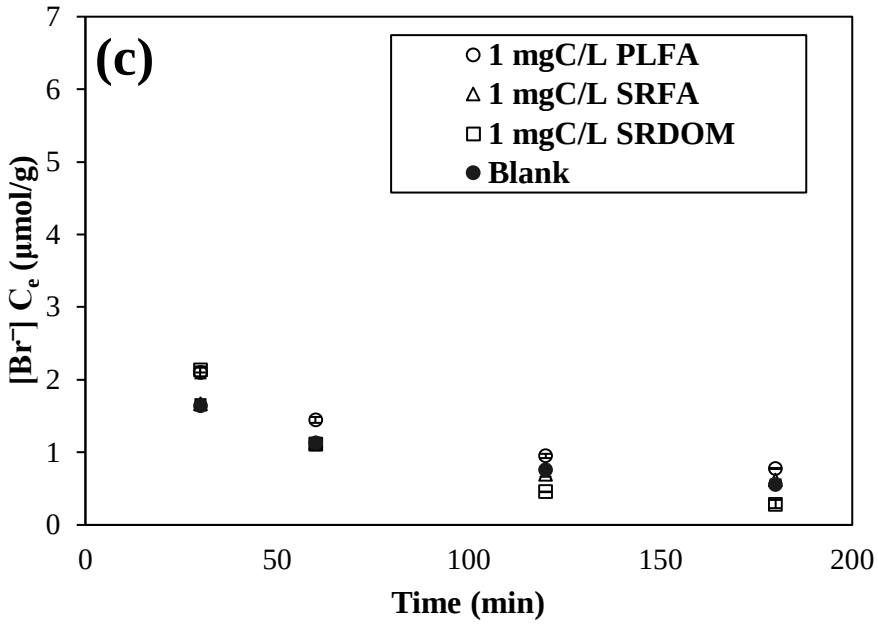


Figure 5-2: Bromide uptake behaviour of SIAC in control sample (without the presence of organics) and in the presence of 1mgC/L of different NOM isolates at SIAC concentrations of (a) 0.5, (b) 1 and (c) 2 g/L. Initial bromide concentration: 1mg/L (12.5 µM).

The bromide removal process was found to be fast within 30 minutes after the jar test commenced, slowing over time until a steady state was achieved after 180 min. The kinetic data indicated that there was no significant change in equilibrium concentration after this time, up to 6 h. Therefore, the bromide residual concentrations are reported for the samples taken after 30, 60, 120 and 180 min. The capacity of SIAC for sorption of Br^- by addition of NOM to the solution was assessed by conducting blank experiments with no NOM isolates presented in the solution. For all the solutions, the higher contact time resulted in a higher bromide uptake or a lower Br^- residual in solution. Also, increasing the SIAC dosage from 0.5 to 2 g/L significantly improved the bromide removal process from the solution, presumably due to increasing the concentration of available silver sites on SIAC to react with bromide. All types of NOM isolates showed interfering effects in terms of decreasing the bromide removal through SIAC. At the lowest SIAC dosage (0.5 g/L) the bromide residual was reduced by only 60% at 1 mgC/L PLFA while this amount was increased to above 90% in the absence of NOM isolates. The decrease in Br^- uptake upon NOM addition can be attributed to the inactivation of silver sites caused by either electrostatic attraction of

NOM molecules to the SIAC surface or the detachment of Ag^+ from SIAC because of direct bonding interactions to the electron donating groups of NOM molecules.

5.4.3 Role of NOM Type on DOC Removal by SIAC

Changes in NOM nature and chemical composition demonstrated distinguishable effects on bromide removal. Under the experimental conditions in this study, the presence of SRFA and SRDOM resulted in a lower bromide residual compared to that of PLFA. PLFA is rich in sites with higher affinity for Ag^+ (due to high sulphur and nitrogen content) compared to those in SRFA and SRDOM which are largely carboxylic acids and phenols (Gunsolus et al. 2015).

Studies on the effect of SIAC amounts on the extent of DOC removal showed that the extent of DOC removal by SIAC increased with increasing SIAC dosage, as would be expected (Figure 5-3a). For example, a removal range of 20 – 50% using 2 g/L of SIAC was obtained compared to 0 – 10% at 0.5 g/L of SIAC, clearly attributable to increases in total surface area to adsorb NOM molecules (Pelekani et al. 1999; Li 2003; Ding et al. 2008). The SRFA representing the highest $SUVA_{254}$ value among other NOM isolates (Table 5-1) potentially would have the highest reactivity amongst other NOM isolates, however, our observations contradict this hypothesis. PLFA was the only NOM type that was removed even at the lowest SIAC dosage (0.5 g/L) by 10%, where neither SRFA nor SRDOM were removed at this SIAC dose. Two scenarios can support the higher adsorption affinity of PLFA molecules towards SIAC: 1) lower molecular weight NOM fractions generally adsorb to a greater extent so that PLFA, which had with the lowest molecular weight distribution may have been adsorbed to a greater extent for this reason (Newcombe 1999; Li 2003). This hypothesis is in agreement with previous research (Newcombe 1997; Newcombe et al. 1997) given that the larger NOM molecules will slowly diffuse through activated carbon pores to reach sorption sites, where smaller NOM molecules reaching the sorption sites, may have already been adsorbed. However, the relatively higher polarity of smaller NOM molecules compared to larger ones may decrease their adsorption capacity on the hydrophobic activated carbon. Apart from charge distribution, the presence of various functional groups on the activated carbon surface can influence the adsorption properties of NOM molecules (Sakuma et al. 2015).

Therefore, another scenario can be related to the higher affinity of PLFA molecules towards available Ag^{+} sites on SIAC which are capable of attracting PLFA reactive sites towards SIAC.

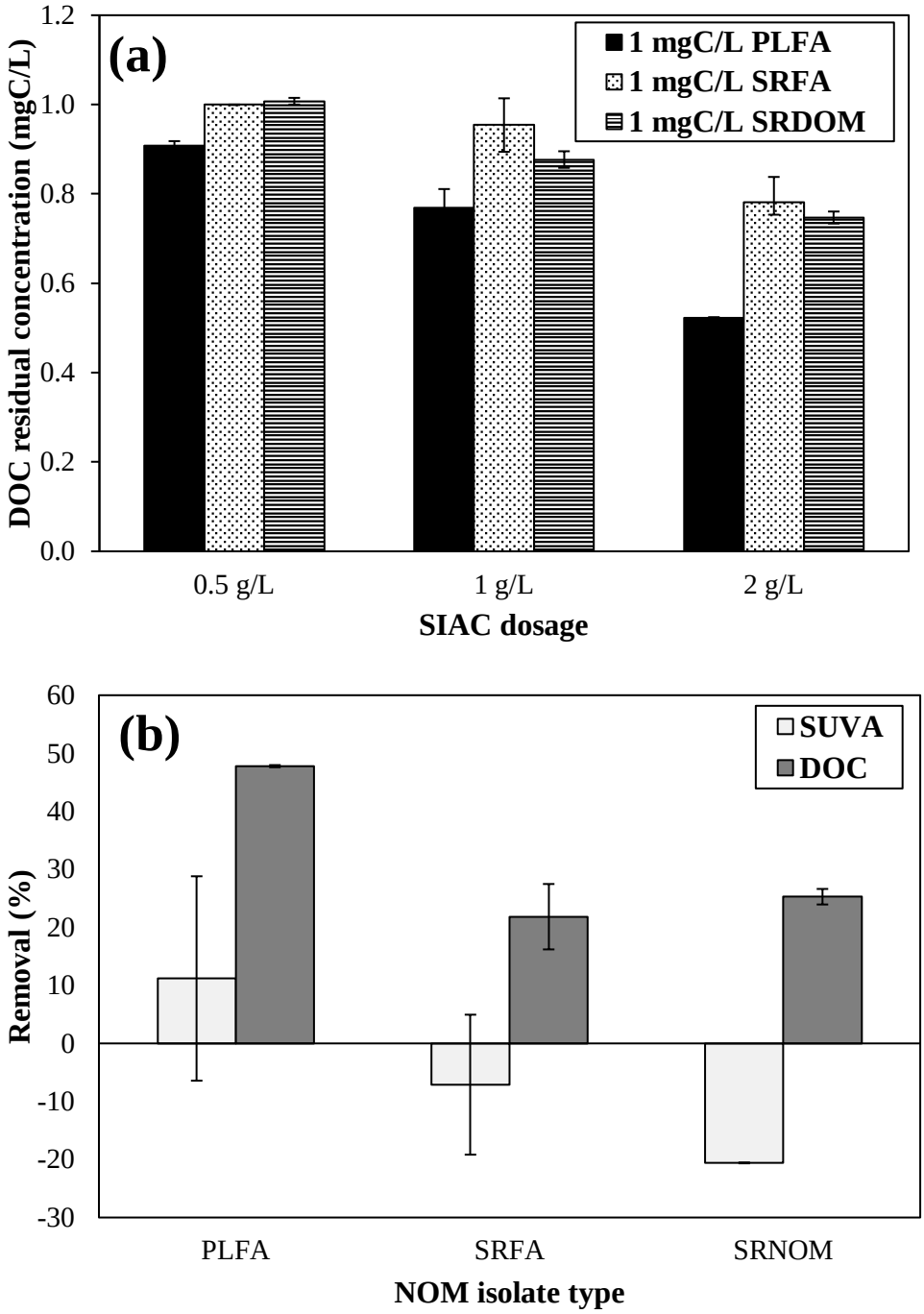


Figure 5-3: (a) Effect of NOM isolate types on DOC residual in bromide solution using 0.1, 1 and 2 g/L of SIAC, (b) DOC and $SUVA_{254}$ removal efficiency using 2 g/L of SIAC. Batch experiment of three hours; Initial bromide concentration: 1 mg/L (12.5 μM); Initial DOC concentration 1 mgC/L

The presence of the significantly higher sulphur and/or nitrogen functionalities in PLFA isolated NOM compared to SRDOM and PLFA (Table 5-1) may be attributable to the greater affinity of PLFA NOM onto SIAC. Our results suggested a greater DOC removal from PLFA containing solutions, presumably corresponded to high affinity of these reactive groups towards Ag^+ available at the SIAC surface. For example, the nitrogen content of the PLFA NOM isolates, a possible indicator of amine ligand groups, was greater in PLFA (6.5% N) compared to SRFA (0.72% N). Likewise, PLFA contained greater sulphur content (3.0% S) compared to SRFA (0.44% S), and about 53−72% of the sulphur comprises reduced-S moieties (such as thiols) that were strong binding sites for silver (Manceau et al. 2012).

Additionally, the $SUVA_{254}$ and DOC removal efficiency of 2 g/L of SIAC for three different NOM extracts was separately depicted in Figure 5-3b. Unlike DOC, the average of $SUVA_{254}$ removal values for all types of NOM extracts were found to be negative. This suggests that low SUVA (non-aromatic) content in NOM extracts was removed in preference to aromatic content for SRFA and SRDOM but not for PLFA. This may be because the UV absorbing material in PLFA is different to the UV-absorbing material in SRFA and SRNOM. This result would suggest that SIAC has low affinity for the adsorption of aromatic fractions of NOM molecules. Similar observations were found where lower NOM removal capacity was obtained for SRFA, with two times higher $SUVA_{254}$ value (5.16) compared to that of PLFA with less aromatic properties (2.51). A recent study also showed that NOM molecules with low $SUVA_{254}$ values and consequently higher hydrophilic fractions induced higher binding capacities and affinities for Ag^+ compared to the corresponding hydrophobic NOM with higher degree of aromaticity (Yoo et al. 2016). It was also found that the increasing the aliphatic and hydrophilic properties can be related to the increasing of N/C ratio in NOM molecules (Cawley et al. 2013; Yoo et al. 2016)

5.4.4 Role of NOM Type on the Extent of Silver Leaching

The effect of NOM composition on the extent of silver leaching was investigated for constant initial concentrations of Br^- (1 mg/L) and NOM isolates (1 mgC/L) at various SIAC doses (Figure 5-4a). Silver leaching results obtained from either blank (with no NOM isolates presented in the solution) or NOM containing experiments are shown

at relatively low dissolved silver values, with the maximum less than 1.5 µmol/g of Ag^+; given that the total amount of silver on the SIAC was previously quantified to be 12.9 µmol/g. However, in order to assess the interfering effects of NOM isolates, the dissolved silver values obtained at 2 g/L of SIAC were plotted separately in Figure 5-4b.

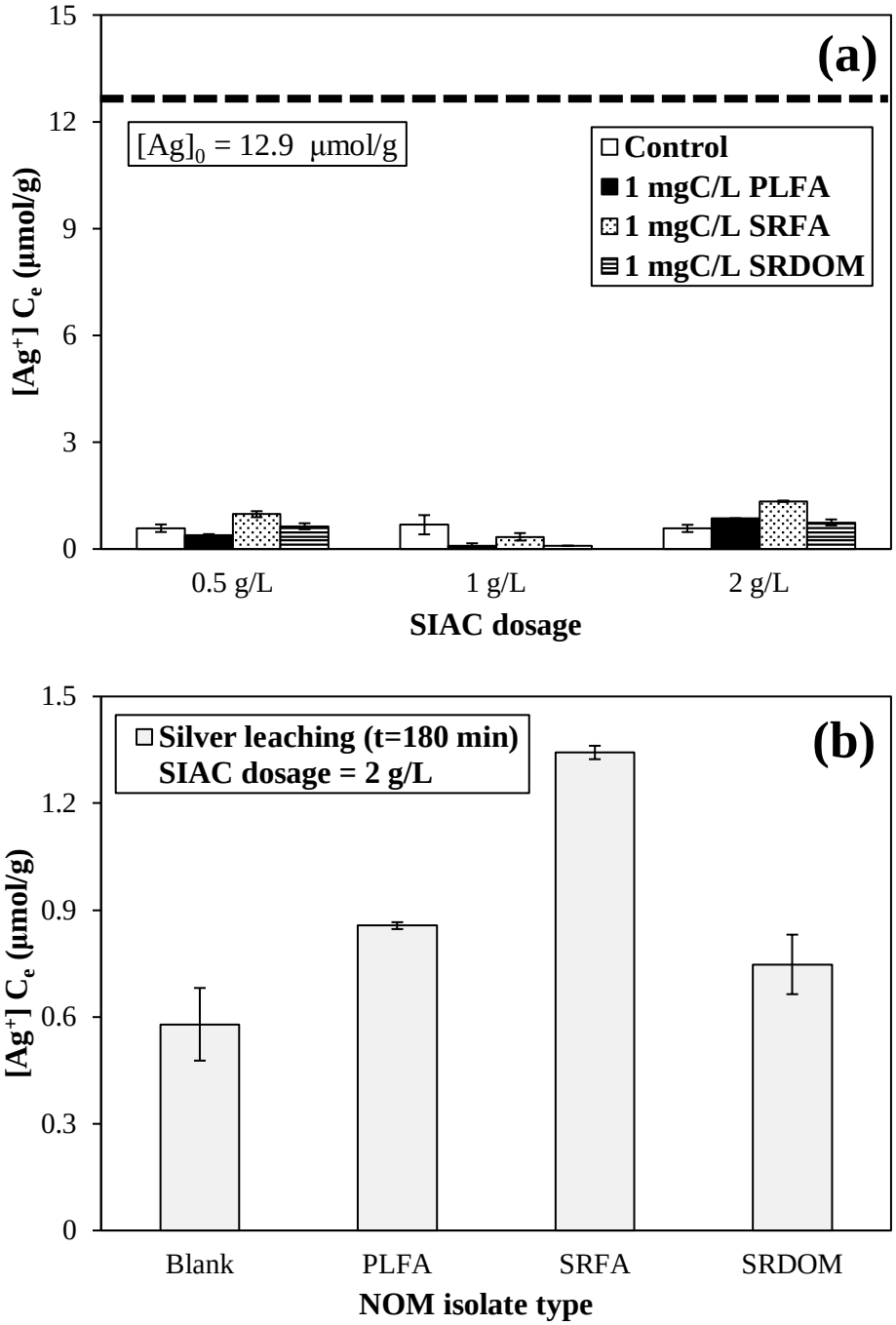


Figure 5-4: (a) Effect of NOM isolate types on silver leaching behaviour in bromide solution using 0.5, 1 and 2 g/L of SIAC, (b) at 2 g/L with different scales. Batch experiment of three hours; Initial bromide concentration: 1 mg/L (12.5 µM); Initial DOC concentration 1 mgC/L

The presence of SRFA induces the highest value of dissolved silver of 1.4 μmol/g, approximately two times higher, compared to that of blank solution. However, in the case of the PLFA and SRDOM an approximately 40% less impact on the extent of silver leaching was observed. These results are also in agreement with previous studies showing that changes in NOM composition may result in a distinguishable difference in Ag^+ speciation as in free Ag^+ or Ag–NOM (Yang et al. 2014; Gunsolus et al. 2015).

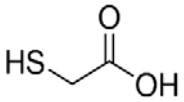
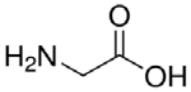
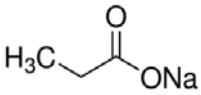
To explain these observations, two types of Ag^+ binding sites can be defined for the studied NOM isolates: weak–binding sites with minor effects on Ag^+ binding to NOM which are mostly composed of oxygen-containing functional groups such as carboxylates and phenols, and strong binding sites with high affinity for Ag^+ that are likely to consist of amine and thiol functional groups (Adegboyega et al. 2013; Yang et al. 2014; Gunsolus et al. 2015). At the pH of our experiments (an average pH of 7.5 ± 0.2) the SIAC surface is negatively charged, in a favourable condition to hold Ag^+ on its surface. In the presence of NOM molecules, the complexation of Ag^+ sites on the SIAC surface with variable NOM types is expected. However, the significant differences of NOM isolates in physical (e.g. average molecular weight, aromaticity) and chemical (e.g. Ag–coordinating functional groups) characteristics may explain our observations to a great extent. Since all types of NOM used in this study are chemically capable of complexation of Ag^+, their chemical characteristics possibly would not explain differences in silver leaching data.

At similar Ag/NOM ratio, a higher average molecular weight of SRFA (> 2200 Da) compared to that of PLFA (1200 – 1400 Da) could possibly initiate the attractive interaction of Ag^+ from the SRFA molecules into the bulk solution (Liu and Hurt 2010). In case of PLFA, the smaller average molecular weight than SRFA as well as the presence of thiol functional groups as the strongest binding sites for Ag^+, protective coverage of SIAC through PLFA molecules and consequently a less silver dissolution is likely to occur. The latter is further supported by the DOC data in Figure 5-3a, indicating the lowest DOC residual values in presence PLFA at every SIAC concentration.

5.4.5 Performance Evaluation of SIAC using Sulphur- and Nitrogen-rich NOM Model Compounds

Due to the complexity of NOM composition used in this study and the uncertainty associated with the molecular characteristics of the samples, identification of mechanisms to explain the influence of the different NOM types on bromide removal using SIAC was difficult. To overcome this issue, three simple organic model compounds with relatively low molecular weights and rich in sulphur or nitrogen were chosen as surrogates for the NOM isolates (Table 5-2). Glycine (G), is the simplest neutral amino acid with equal number of amino and carboxyl groups. It is often regarded as a nonpolar amino acid mainly due to the presence of C–H side chains with negligible dipole-dipole interactions (Shoeib et al. 2002). Thioglycolic acid (TGA) is an analogue of the glycine molecule where nitrogen is replaced by a sulphur atom. TGA was previously used by other researchers as a compound to represent NOM sourced from the degradation of organic detritus derived from algae and bacteria within a wetland environment (Aiken et al. 2003).

Table 5-2: Physiochemical characteristics of NOM model compounds

Compound	Structure	Classification	Binding Sites for Ag^+
Thioglycolic acid (TGA)		neutral, polar	Carboxylic acid, Thiol
Glycine (G)		neutral, nonpolar	Carboxylic acid, Amino acid
Sodium propionate (SP)		hydrophilic neutral	Carboxylic acid

To determine the impact of N– and S–containing model compounds on DOC removal and the role of Ag^+, equimolar sodium propionate (SP) solutions were prepared and used as the control sample. Both TGA and SP indicated significantly high adsorption towards SIAC with more than 90% of DOC removed (Figure 5-5). In the presence of 1 ppm sodium bromide (NaBr), an enhanced adsorption of TGA and SP was observed which can be explained by the partial neutralization of electrostatic repulsion between the adsorbate and the adsorbent (Kilduff et al. 1996; Newcombe et al. 1997). Furthermore, due to the high affinity of sulphur towards the Ag^+ sites on the surface

of SIAC, a slightly higher adsorption of TGA compared to SP is observed. However, in the case of glycine an insignificant adsorption towards SIAC was observed, where the obtained DOC removal was only about 5%. Glycine adsorption was significantly stronger on GAC than that on SIAC, where its DOC removal was increased to above 40%. This increase can be attributed to the greater point of zero of charge of F400 (pH_{PZC} 9.6) than that of SIAC (pH_{PZC} 8.1). At pH 7.5 ± 0.2 at which these experiments were carried out, GAC would become more positively charged in the solution to attract the glycine molecules from their negatively charged carboxylate side. Moreover, by switching from SIAC to F400-GAC, the adsorption of TGA was decreased from above 95% down to about 70%. This would further suggest that the presence of Ag^+ sites on SIAC plays a key role in a more adsorption of sulphur–containing TGA molecules from the solution.

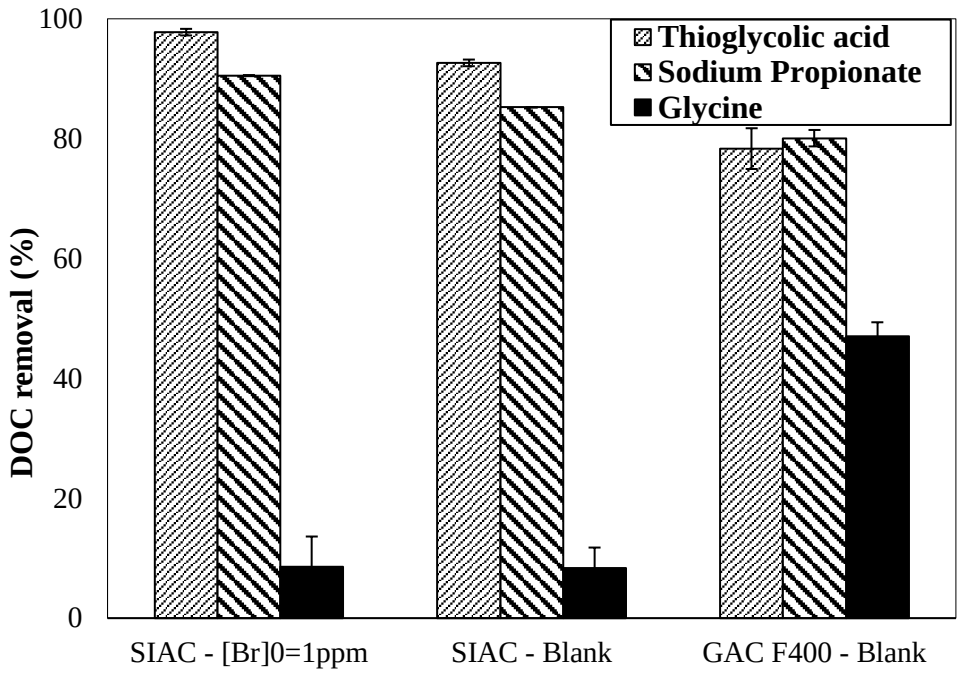


Figure 5-5: Effect of NOM model compounds on DOC removal efficiency in presence and the absence of 1 mg/L of bromide using SIAC and GAC F400

These observations can be further supported based on the distinguishable solubility of Ag^+ complexes corresponding to the various ligands used in this study. Since the SIAC was preconditioned at high pH prior to use, the deposition of AgOH complexes on the surface of SIAC is expected. The dissociation constant (K_d) for Ag^+–G and Ag^+–TGA complexes are calculated based on their stability constant (K_f) reported elsewhere so

that the K_d is an inverse value of K_f (Smith et al. 1998). At the Ag^+ /ligand ratio > 1, the Ag^+–ligand complex formation reactions are proposed to proceed as follows:

$$Ag^+ + OH^- \rightleftarrows AgOH \qquad K_{sp} = 1.52 \times 10^{-8} \qquad (5.2)$$

$$Ag(I)-G \rightleftarrows Ag^+ + H_2N-CH_2-COOH \qquad K_d = 1.28 \times 10^{-7} \qquad (5.3)$$

$$Ag(I)-TGA \rightleftarrows Ag^+ + SH-CH_2-COOH \qquad K_d = 1.58 \times 10^{-15} \qquad (5.4)$$

Due to the higher stability (lower solubility) of silver hydroxide at the surface of SIAC, the formation potential for the Ag-glycine complexes would be less possible, therefore, the adsorption of glycine on SIAC was observed to be very limited. Due to the significantly lower solubility of Ag–TGA compared to silver hydroxide (AgOH), strong binding of mercaptans (thiol groups) from TGA towards SIAC was observed. To further understand the adsorption properties of SIAC, bromide removal was also monitored at a lower molar ratio of model compounds to silver. Figure 5-6a shows a time dependant bromide residual in solution which initially contained 15 and 12.5 µM of model compounds and bromide, respectively. At each of the sampling intervals, it appeared that the presence of TGA had the highest inhibition on bromide uptake through SIAC. Under these conditions, glycine had a significantly lower interfering effect on the bromide removal properties of SIAC compared to that of TGA, where the bromide residual values decreased by 35%. Together with results showed in Figure 5-2, it would be assumed that NOM molecules (and organic model compounds) containing the highest S/C ratio are potentially important in SIAC stability and its bromide removal performance.

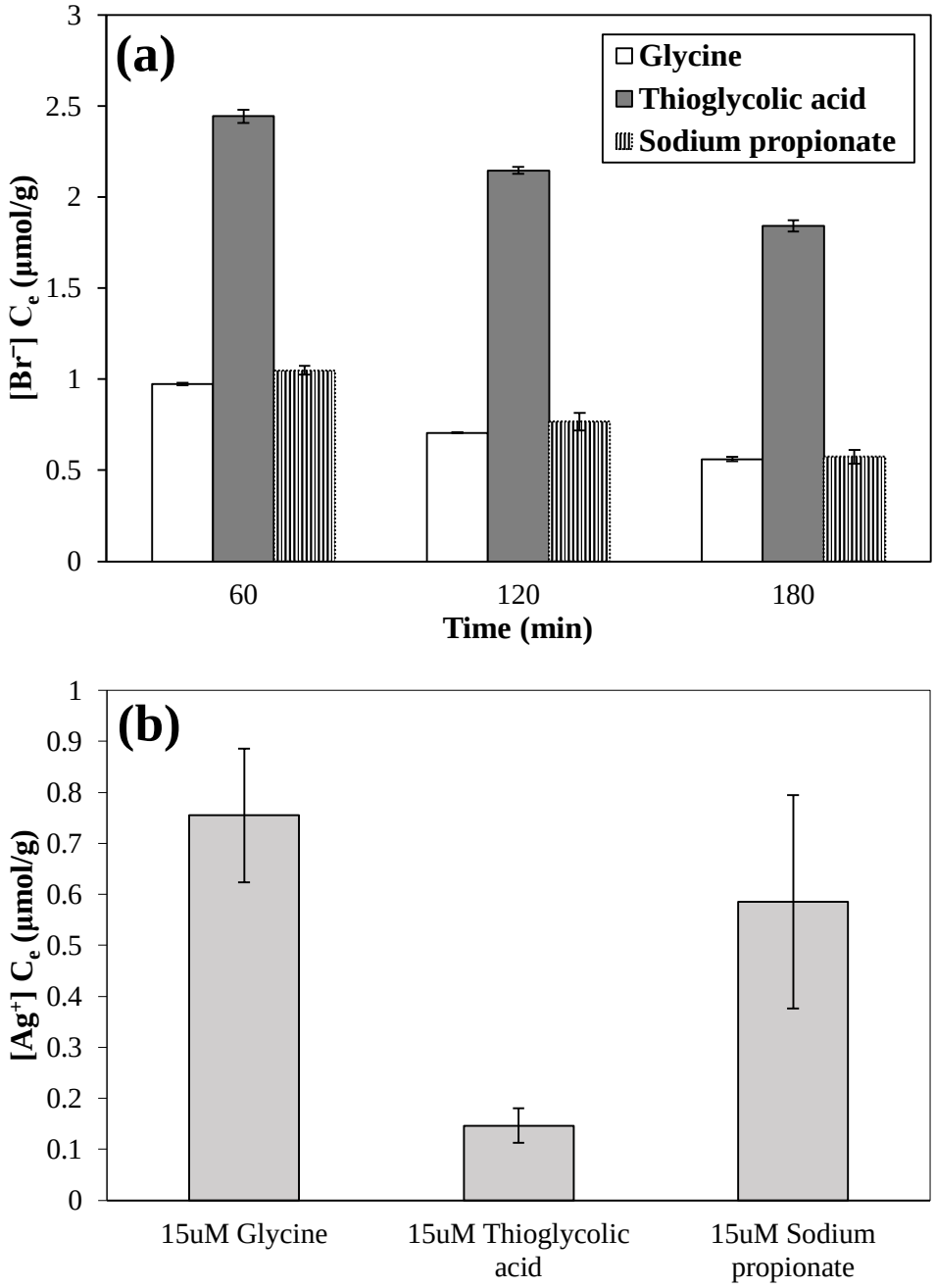


Figure 5-6: Effect of different NOM model compounds on (a) bromide uptake and (b) silver leaching from 2 g/L of SIAC. I Batch experiment of three hours; Initial bromide concentration: 1 mg/L (12.5 µM); Initial NOM model compounds concentrations: 15 µM

Silver leaching was also affected differently by the different functional groups on organic molecules (Figure 5-6b). The relative impact of the functionalities of NOM model compounds on the extent of silver leaching is qualitatively consistent with the silver leaching results obtained for the NOM isolates (Figure 5-4b). As a whole, the presence of organics rich in sulphur content reduced the extent of silver leaching from

SIAC. Along with the corresponding DOC removal obtained for the thioglycolic acid (Figure 5-5), it is suggested that due to the adsorption of dissolved organic molecules containing appreciable amounts of thiol functionalities in a great extent to SIAC, Ag^+ sites would be covered and inactivated. As a result, the extent of silver leaching would be decreased while the DOC removal is enhanced.

5.5 Conclusions

Previous feasibility studies into the application of SIAC for halide removal reported on the apparently conflicting hypotheses regarding the interpretation of NOM effects on the bromide removal capacity of SIAC. This study suggested that interferences caused by the coexistence of NOM molecules cannot be fully attributed to the physical characteristics of NOM such as aromaticity (e.g. $SUVA_{254}$). Our data suggested that the chemical composition of NOM plays an important role in determining the extent of bromide removal and silver leaching of SIAC. Due to significantly higher electron donating groups such as sulphur and nitrogen functionalities compared to other NOM extracts, a higher possibility of complexation reactions of Ag^+ (chemisorbed on the SIAC) is expected. Furthermore, PLFA which has a weight-averaged molecular weight between 1200 and 1400 Da, the smallest compared to other NOM extracts, would have the greatest propensity to enter and to physically adsorb within to the smaller pores of SIAC. The findings obtained from NOM extracts were further supported by experiments using small model compounds including glycine (nitrogen-rich), thioglycolic acid (sulphur–rich) and sodium propionate (blank). The presence of the sulphur–rich organic model compound, thioglycolic acid lowered the bromide removal efficiency from > 95 to 60%, corresponding to the inactivation of SIAC adsorption sites by direct complexation Ag^+ with sulfhydryl electron donating groups. In contrast to thioglycolic acid, glycine did not significantly reduce the bromide removal capacity while the extent of silver leaching was increased, probably due to the significantly lower solubility of silver bromide (5.2×10^{-13}) compared to that of silver-glycine (1.28×10^{-7}). Therefore, the anion exchange of glycine for bromide is expected to occur. As a result, an alternative bromide removal pathway can be considered through glycine complexation dissolution of Ag^+ followed by the bromide-glycine anion exchange reaction.

Chapter 6

Conclusions and Recommendations

The primary objective of this PhD study was to progress the development of an adsorption process utilising silver-impregnated activated carbon (SIAC) for the selective bromide removal from water. Adsorption using SIAC had been shown to be a promising option in previous studies and the fact that this technology is potentially retrofittable to conventional existing treatment plants makes it attractive.

Three separate adsorption studies were applied for the qualitative assessment of the SIAC adsorbents. First, a feasibility study was carried out which confirmed previous studies that SIAC adsorbents are highly efficient in the removal of bromide at concentrations relevant to drinking source waters and that use of fresh GAC also appeared to remove appreciable concentrations of bromide. Additionally, several other factors that have not been considered in previous studies such as the kinetics of bromide adsorption and the leaching of silver from SIAC into the treated water, were also assessed. More than 66% removal of bromide was observed after the first 30 minutes of the controlled experiment, where no other interfering species existed. However, after 180 minutes, the rate for the bromide removal slowed down, which could be attributable to the reduction of available adsorption sites. Langmuir and Freundlich isotherms were used to analyse bromide uptake data for a contact time of 180 min. It was found that the bromide removal properties of the fresh SIAC can be predicted by the Freundlich model. However, for the second and third adsorption experiments using the same batch of SIAC, the Langmuir isotherm showed an improved fit for the bromide uptake data. This suggests that the sorption of Br^- onto SIAC is likely to involve precipitation reactions between the Ag^+ sites on the SIAC and Br^- species in the solution. Assuming the multilayer adsorption theory (Freundlich theory), the AgBr precipitation reaction is likely to occur and will continue until all available silver has reacted. Superior bromide removal was achieved in pure water, in the absence of organic and inorganic interferences, but significant removal was still achieved for the SIAC treatment of a real water samples containing 0.155 and 3.37 mg/L of initial bromide and DOC, respectively. It was observed that the bromide and DOC removal efficiencies were both above 60% after 180 min of the contact. However, the $SUVA_{254}$ value, which indicates the extent of aromaticity in DOC, was found to increase after this SIAC treatment. This suggests that the SIAC has a preferential affinity for the adsorption of non-aromatic fractions of NOM.

Unlike previous research where the silver leaching properties of SIAC were not studied in detail, our study focused on several factors determining the practicalities of the use of SIAC for bromide removal, including the kinetics of bromide adsorption and, in particular, the leaching of silver from the SIAC into the treated water. The SIAC showing the highest bromide removal efficiency was subjected to further studies on the impact of SIAC preconditioning on the bromide removal capacity and minimisation of silver leaching. It was found that preconditioning at pH above 10 decreased the release of Ag^+ and immobilised silver halides by 40% and that it did not deteriorate the capacity of SIAC to remove bromide. Also, preconditioning in 1 mM of perchlorate solution at pH 8.2 significantly reduced the silver loss from 40% to about 16%. Comparing the initial silver coatings between both types of preconditioned SIAC revealed that SIAC treatment at high pH (10.4) was more beneficial to minimise loss of silver, while preconditioning in mild alkaline solution (pH 8.2) did not lead to a significant reduction in silver leaching. Overall, the study indicated that the preconditioning of SIAC at high pH has high potential to alter the bromide and silver interaction from an unwanted aqueous phase precipitation reaction to a desirable chemisorption mechanism occurring on the surface of SIAC. To achieve a better understanding of the practical implications of preconditioning on this type of SIAC, a natural water matrix was tested using both pristine SIAC and SIAC preconditioned at pH 10.4. Silver leaching and bromide removal using both pristine and preconditioned SIAC at pH 10.4 in the presence of dissolved chloride (Br^-/Cl^- ratio of 1:300 by weight) and in a real water sample were determined. It was shown that chloride has the most interfering role, reducing the bromide removal efficiency as well as the extent of silver leaching from the SIAC during the first three hours of the test. Both pristine and preconditioned SIAC removed NOM as well as bromide but the pristine SIAC had a slightly improved NOM removal capacity after contact times greater than 24 hours.

Previous studies of the application of SIAC for the bromide removal reported conflicting hypotheses regarding the interpretation of the effect of NOM on the bromide removal capacity of SIAC. This study suggested that interferences caused by the coexistence of NOM molecules cannot be fully attributed to characteristics such as aromaticity (e.g. $SUVA_{254}$). Other NOM chemical compositional characteristics also affected the performance of SIAC in the removal of bromide, removal of organic

carbon and leaching of silver. Pony Lake fulvic acid (PLFA), the NOM extract with the highest concentrations of electron donating groups such as sulphur and nitrogen functionalities, was found to be the most interfering in terms of decreasing the adsorption of bromide onto the SIAC. Interaction between silver sites on the SIAC and sulphur and nitrogen containing groups in PLFA molecules was considered as the main reason for the reduced bromide removal. Additionally, the DOC removal results showed that PLFA molecules had been significantly adsorbed onto the SIAC. Since the PLFA was reported as having the lowest weight-average molecular compared to the other NOM extracts, it would be expected that these small molecules could be removed by inclusion into the pores within the SIAC. The findings obtained from studies using NOM extracts were further supported by studies with small model compounds including glycine (nitrogen-rich), thioglycolic acid (sulphur–rich) and sodium propionate (control). The presence of the sulphur–rich organic model compound, thioglycolic acid lowered the bromide removal efficiency from >95% to 60%. This was probably due to the inactivation of SIAC adsorption sites by direct complexation of Ag^{+} with sulfhydryl electron donating groups. In contrast to thioglycolic acid, the presence of glycine did not significantly reduce the bromide removal capacity but glycine did increase the extent of silver leaching. This was most likely due to the significantly lower solubility of silver bromide (5.2×10^{-13}) compared to that of silver-glycine (1.28×10^{-7}). Therefore, anion exchange of glycine for bromide is expected to occur. As a result, an alternative bromide removal pathway can be considered through glycine complexation dissolution of Ag^{+} followed by the bromide-glycine anion exchange reaction.

The outcomes of this research can be advantageous for the water industry in terms of reducing bromide-related problems, in terms of both aesthetic (tastes and odours and manganese-related discoloured water events) and health aspects. This technique for bromide removal will also have beneficial impacts in rural and remote locations in Australia, where marginal quality water supplies are used, which often contain elevated bromide levels. Minimisation of bromide will also lead to decreased formation of disinfection by-products and better control of disinfectant residuals, improving risk management for water utilities. Moreover, the results of this research suggest that additional future work to further understand the occurrence and

minimisation of DBPs after SIAC treatment strategies is required. Recommendations for further research are summarised below:

Further research on SIAC treatment is required on the potential for regeneration and economic feasibility of using this treatment on a large scale, and the lifetime of the activated carbon beds before halide breakthrough is experienced. Use of kinetic and isotherm data from this study would help to develop and model an industrial scale adsorption system based on SIAC that is retrofittable and suitable for implementation within an existing conventional water treatment process. It is also important to test the performance of SIAC for the treatment of Australian source waters to develop understanding of the effects of the local water matrix on bromide adsorption by SIAC. In addition, previous studies have determined the performance of SIAC in minimising selected, mainly regulated, DBPs rather than for the full suite of halogenated organic compounds as measured by AOCl and AOBr measurements. Therefore, identifying the research gaps and improving understanding of how SIAC treatment can minimise the formation of total brominated-DBPs (AOBr) is also important in the development of this treatment process.

Layered double hydroxides (LDHs) and natural zeolite have been shown to have a high capacity to adsorb anions through a combination of ion exchange and ion inclusion mechanisms. There exists a wide variety of natural zeolites across Australia and these materials could potentially be locally applied. A further advantage of LDHs and zeolites is their chemical and thermal stability either during the adsorption or regeneration point-of-use. LDHs and zeolites have not been thoroughly investigated for water treatment applications, and there are many unknowns concerning mass transfer processes during the adsorption of anions from the bulk solution. There is potential for further developments to be made through synthesis or modification of LDHs and zeolite e.g. through silver impregnation to achieve faster adsorption kinetics and greater sorption capacity.

References

Acero, J. L., Piriou, P. and von Gunten, U., 2005. Kinetics and mechanisms of formation of bromophenols during drinking water chlorination: assessment of taste and odor development. Water research. 39(13), pp. 2979–93.

Adegboyega, N. F., Sharma, V. K., Siskova, K., Zbořil, R., Sohn, M., Schultz, B. J. and Banerjee, S., 2013. Interactions of Aqueous Ag^{+} with Fulvic Acids: Mechanisms of Silver Nanoparticle Formation and Investigation of Stability. Environmental Science & Technology. 47(2), pp. 757–764.

Aiken, G., Haitzer, M., Ryan, J. N. and Nagy, K., 2003. Interactions between dissolved organic matter and mercury in the Florida Everglades. Journal De Physique Iv.

Ali, I. and Gupta, V. K., 2006. Advances in water treatment by adsorption technology. Nature protocols. 1(6), pp. 2661–7.

Allard, S., Fouche, L., Dick, J., Heitz, A. and von Gunten, U., 2013. Oxidation of manganese(II) during chlorination: role of bromide. Environmental science & technology. 47(15), pp. 8716–23.

Allard, S., Nottle, C. E., Chan, A., Joll, C. and von Gunten, U., 2013. Ozonation of iodide-containing waters: Selective oxidation of iodide to iodate with simultaneous minimization of bromate and I-THMs. Water Research. 47(6), pp. 1953–1960.

Allard, S., Tan, J., Joll, C. A. and von Gunten, U., 2015. Mechanistic Study on the Formation of Cl-/Br-/I-Trihalomethanes during Chlorination/Chloramination Combined with a Theoretical Cytotoxicity Evaluation. Environmental Science & Technology. 49(18), pp. 11105–11114.

Andelman, M. and Walker, G., 2004. Charge barrier flow-through capacitor. U.S. Patent 6,709,560.

Ando, N., Matsui, Y., Kurotobi, R., Nakano, Y., Matsushita, T. and Ohno, K., 2010. Comparison of natural organic matter adsorption capacities of super-powdered activated carbon and powdered activated Carbon. Water Research. 44(14), pp. 4127–4136.

Ates, N., Yetis, U. and Kitis, M., 2007. Effects of Bromide Ion and Natural Organic Matter Fractions on the Formation and Speciation of Chlorination By-Products. Journal of Environmental Engineering. 133(10), pp. 947–954.

Banasiak, L. J. and Schäfer, A. I., 2009. Removal of inorganic trace contaminants by electrodialysis in a remote Australian community. Desalination. 248(1–3), pp. 48–57.

Bandyopadhyaya, R., Sivaiah, M. V. and Shankar, P. A., 2008. Silver -embedded granular activated carbon as an antibacterial medium for water purification. Journal of Chemical Technology & Biotechnology. 83(8), pp. 1177–1180.

Bartels, C., Rybar, S. and Andes, K., 2009. Optimized removal of boron and other specific contaminants by SWRO membranes. IDA World Congress-Dubai UAE. 9, pp. 7–12.

Baumgartner, J., Murcott, S. and Ezzati, M., 2007. Reconsidering 'appropriate technology': the effects of operating conditions on the bacterial removal performance of two household drinking-water filter systems. Environmental Research Letters. 2(2), p. 24003.

Beck, C. B., 1973. Physicochemical processes for water quality control, Walter J. Weber, Jr.(with eight contributors), Interscience, New York(1972) 640 pages. AIChE Journal. 19(2), pp. 413–413.

Bell Jr, F. A., 1991. Review of effects of silver-impregnated carbon filters on microbial water quality. Journal (American Water Works Association). pp. 74–76.

Benarde, M. A., Israel, B. M., Olivieri, V. P. and Granstrom, M. L., 1965. Efficiency of Chlorine Dioxide as a Bactericide. Appl. Envir. Microbiol. 13(5), pp. 776–780.

Benn, T. M. and Westerhoff, P., 2008. Nanoparticle Silver Released into Water from Commercially Available Sock Fabrics. Environmental Science & Technology. 42(11), pp. 4133–4139.

Biesheuvel, P. M. and van der Wal, A., 2010. Membrane capacitive deionization. Journal of Membrane Science. 346(2), pp. 256–262.

Bousher, A., Brimblecombe, P. and Midgley, D., 1986. Rate of hypobromite formation in chlorinated seawater. Water Research. 20(7), pp. 865–870.

Boyer, T. H. and Singer, P. C., 2005. Bench-scale testing of a magnetic ion exchange resin for removal of disinfection by-product precursors. Water Research. 39(7), pp. 1265–1276.

Boyer, T. H., Singer, P. C. and Aiken, G. R., 2008. Removal of Dissolved Organic Matter by Anion Exchange: Effect of Dissolved Organic Matter Properties. Environmental Science & Technology. 42(19), pp. 7431–7437.

Bratby, J., 2016. Coagulation and flocculation in water and wastewater treatment, IWA Publishing.

Brodtmann, N. V and Russo, P., 1979. The use of chloramine for reduction of trihalomethanes and disinfection of drinking water. Journal (American Water Works Association). pp. 40–42.

Brown, A., McKnight, D. M., Chin, Y.-P., Roberts, E. C. and Uhle, M., 2004. Chemical characterization of dissolved organic material in Pony Lake, a saline coastal pond in Antarctica. Marine Chemistry. 89(1–4), pp. 327–337.

Brown, J. and Sobsey, M. D., 2010. Microbiological effectiveness of locally produced ceramic filters for drinking water treatment in Cambodia. Journal of Water and Health. 8(1), pp. 1–10.

Buffle, M.-O. and Gunten, U. von, 2006. Phenols and Amine Induced HO• Generation During the Initial Phase of Natural Water Ozonation.

Cachafeiro, S. P., Naveira, I. M. and García, I. G., 2007. Is copper–silver ionisation safe and effective in controlling legionella? Journal of Hospital Infection. 67(3), pp. 209–216.

Cawley, K. M., McKnight, D. M., Miller, P., Cory, R., Fimmen, R. L., Guerard, J., Dieser, M., Jaros, C., Chin, Y.-P. and Foreman, C., 2013. Characterization of

fulvic acid fractions of dissolved organic matter during ice-out in a hyper-eutrophic, coastal pond in Antarctica. Environmental Research Letters. 8(4), p. 45015.

Chang, E. E., Lin, Y. P. and Chiang, P. C., 2001. Effects of bromide on the formation of THMs and HAAs. Chemosphere. 43(8), pp. 1029–1034.

Chellam, S., 2000. Effects of nanofiltration on trihalomethane and haloacetic acid precursors removal and speciation in waters containing low concentrations of bromide ion. Environmental Science and Technology. 34(9), pp. 1813–1820.

Chen, C., Apul, O. G. and Karanfil, T., 2017. Removal of bromide from surface waters using silver impregnated activated carbon. Water Research. 113, pp. 223–230.

Chiang, P.-C., Chang, E.-E., Chang, P.-C. and Huang, C.-P., 2009. Effects of pre-ozonation on the removal of THM precursors by coagulation. Science of The Total Environment. 407(21), pp. 5735–5742.

Chin, Y.-P., Aiken, G. and O'Loughlin, E., 1994. Molecular Weight, Polydispersity, and Spectroscopic Properties of Aquatic Humic Substances. Environmental Science & Technology. 28(11), pp. 1853–1858.

Chitrakar, R., Tezuka, S., Sonoda, A., Sakane, K. and Hirotsu, T., 2008. A New Method for Synthesis of Mg−Al, Mg−Fe, and Zn−Al Layered Double Hydroxides and Their Uptake Properties of Bromide Ion. Industrial & Engineering Chemistry Research. 47(14), pp. 4905–4908.

Chubar, N., 2011. New inorganic (an)ion exchangers based on Mg-Al hydrous oxides: (alkoxide-free) sol-gel synthesis and characterisation. Journal of colloid and interface science. 357(1), pp. 198–209.

Chubar, N. I., Samanidou, V. F., Kouts, V. S., Gallios, G. G., Kanibolotsky, V. A., Strelko, V. V and Zhuravlev, I. Z., 2005. Adsorption of fluoride, chloride, bromide, and bromate ions on a novel ion exchanger. Journal of colloid and interface science. 291(1), pp. 67–74.

Criquet, J., Allard, S., Salhi, E., Joll, C. A., Heitz, A. and von Gunten, U., 2012. Iodate and Iodo-Trihalomethane Formation during Chlorination of Iodide-Containing Waters: Role of Bromide. Environmental Science & Technology. 46(13), pp. 7350–7357.

Criquet, J., Allard, S., Salhi, E., Joll, C. A., Heitz, A. and von Gunten, U., 2012. Iodate and Iodo-Trihalomethane Formation during Chlorination of Iodide-Containing Waters: Role of Bromide. Environmental Science & Technology. 46(13), pp. 7350–7357.

Criquet, J., Rodriguez, E. M., Allard, S., Wellauer, S., Salhi, E., Joll, C. A. and von Gunten, U., 2015. Reaction of bromine and chlorine with phenolic compounds and natural organic matter extracts – Electrophilic aromatic substitution and oxidation. Water Research. 85, pp. 476–486.

Criquet, J., Rodriguez, E. M., Allard, S., Wellauer, S., Salhi, E., Joll, C. A. and von Gunten, U., 2015. Reaction of bromine and chlorine with phenolic compounds and natural organic matter extracts – Electrophilic aromatic substitution and oxidation. Water Research. 85, pp. 476–486.

Cunningham, J. H., Cunningham, C., Van Aken, B. and Lin, L.-S., 2008. Feasibility of disinfection kinetics and minimum inhibitory concentration determination on bacterial cultures using flow cytometry. Water Science and Technology. 58(4), pp. 937–944.

Dankovich, T. A. and Gray, D. G., 2011. Bactericidal Paper Impregnated with Silver Nanoparticles for Point-of-Use Water Treatment. Environmental Science & Technology. 45(5), pp. 1992–1998.

Dankovich, T. A. and Gray, D. G., 2011. Bactericidal Paper Impregnated with Silver Nanoparticles for Point-of-Use Water Treatment. Environmental Science & Technology. 45(5), pp. 1992–1998.

Ding, L., Snoeyink, V. L., Mariñas, B. J., Yue, Z. and Economy, J., 2008. Effects of Powdered Activated Carbon Pore Size Distribution on the Competitive Adsorption of Aqueous Atrazine and Natural Organic Matter. Environmental

Science & Technology. 42(4), pp. 1227–1231.

Ding, L., Snoeyink, V. L., Mariñas, B. J., Yue, Z. and Economy, J., 2008. Effects of Powdered Activated Carbon Pore Size Distribution on the Competitive Adsorption of Aqueous Atrazine and Natural Organic Matter. Environmental Science & Technology. 42(4), pp. 1227–1231.

Dobias, J. and Bernier-Latmani, R., 2013. Silver Release from Silver Nanoparticles in Natural Waters. Environmental Science & Technology. 47(9), pp. 4140–4146.

Duirk, S. E., Tarr, J. C. and Collette, T. W., 2008. Chlorpyrifos Transformation by Aqueous Chlorine in the Presence of Bromide and Natural Organic Matter. Journal of Agricultural and Food Chemistry. 56(4), pp. 1328–1335.

Echigo, S., Itoh, S. and Kuwahara, M., 2007. Bromide removal by hydrotalcite-like compounds in a continuous system. 56(11), pp. 117–122.

Echigo, S., Itoh, S. and Kuwahara, M., 2007. Bromide removal by hydrotalcite-like compounds in a continuous system. Water science and technology : a journal of the International Association on Water Pollution Research. 56(11), pp. 117–22.

Farkas, L., Lewin, M. and Bloch, R., 1949. The Reaction between Hypochlorite and Bromides. Journal of the American Chemical Society. 71(6), pp. 1988–1991.

Ferro-García, M. A., Rivera-Utrilla, J., Bautista-Toledo, I. and Moreno-Castilla, C., 1998. Adsorption of Humic Substances on Activated Carbon from Aqueous Solutions and Their Effect on the Removal of Cr(III) Ions. Langmuir. 14(7), pp. 1880–1886.

Flury, M. and Papritz, A., 1993. Bromide in the Natural Environment: Occurrence and Toxicity. Journal of Environment Quality. 22(4), p. 747.

Friberg, L., 1956. QUANTITATIVE STUDIES ON THE REACTION OF CHLORINE WITH BACTERIA IN WATER DISINFECTION. Acta Pathologica Microbiologica Scandinavica. 38(2), pp. 135–144.

Gabelich, C. J., Tran, T. D. and Suffet, I. H. “Mel,” 2002. Electrosorption of

Inorganic Salts from Aqueous Solution Using Carbon Aerogels. Environmental Science & Technology. 36(13), pp. 3010–3019.

Gangadharan, D., Harshvardan, K., Gnanasekar, G., Dixit, D., Popat, K. M. and Anand, P. S., 2010. Polymeric microspheres containing silver nanoparticles as a bactericidal agent for water disinfection. Water Research. 44(18), pp. 5481–5487.

Ge, F., Shu, H. and Dai, Y., 2007. Removal of bromide by aluminium chloride coagulant in the presence of humic acid. Journal of hazardous materials. 147(1–2), pp. 457–62.

Ge, F. and Zhu, L., 2008. Effects of coexisting anions on removal of bromide in drinking water by coagulation. Journal of hazardous materials. 151(2–3), pp. 676–81.

Glaze, W. H., Kang, J.-W. and Chapin, D. H., 1987. The Chemistry of Water Treatment Processes Involving Ozone, Hydrogen Peroxide and Ultraviolet Radiation. Ozone: Science & Engineering. 9(4), pp. 335–352.

Gong, C., Zhang, Z., Qian, Q., Liu, D., Cheng, Y. and Yuan, G., 2013. Removal of bromide from water by adsorption on silver-loaded porous carbon spheres to prevent bromate formation. Chemical Engineering Journal. 218, pp. 333–340.

Goodwill, J. E., Jiang, Y., Reckhow, D. A., Gikonyo, J. and Tobiason, J. E., 2015. Characterization of Particles from Ferrate Preoxidation. Environmental Science & Technology. 49(8), pp. 4955–4962.

Gruchlik, Y., Tan, J., Allard, S., Heitz, A., Bowman, M., Halliwell, D., Gunten, U., Criquet, J. and Joll, C., 2015. Impact of bromide and iodide during drinking water disinfection and potential treatment processes for their removal or mitigation. Water. 41(8), pp. 38–43.

Gu, B., Brown, G. M., Maya, L., Lance, M. J. and Moyer, B. A., 2001. Regeneration of Perchlorate (ClO 4 -)-Loaded Anion Exchange Resins by a Novel Tetrachloroferrate (FeCl 4 -) Displacement Technique. Environmental Science & Technology. 35(16), pp. 3363–3368.

Gunsolus, I. L., Mousavi, M. P. S., Hussein, K., Bühlmann, P. and Haynes, C. L., 2015. Effects of Humic and Fulvic Acids on Silver Nanoparticle Stability, Dissolution, and Toxicity. Environmental Science & Technology. 49(13), pp. 8078–8086.

von Gunten, U., 2003. Ozonation of drinking water: Part II. Disinfection and by-product formation in presence of bromide, iodide or chlorine. Water Research. 37(7), pp. 1469–1487.

von Gunten, U. and Hoigne, J., 1994. Bromate Formation during Ozonization of Bromide-Containing Waters: Interaction of Ozone and Hydroxyl Radical Reactions. Environmental Science & Technology. 28(7), pp. 1234–1242.

von Gunten, U. and Oliveras, Y., 1998. Advanced Oxidation of Bromide-Containing Waters: Bromate Formation Mechanisms. 32(1), pp. 63–70.

Haag, W. R. and Hoigne, J., 1983. Ozonation of bromide-containing waters: kinetics of formation of hypobromous acid and bromate. Environmental Science & Technology. 17(5), pp. 261–267.

Hale, A., 1918. The applications of electrolysis in chemical industry.

van Halem, D., van der Laan, H., Heijman, S. G. J., van Dijk, J. C. and Amy, G. L., 2009. Assessing the sustainability of the silver-impregnated ceramic pot filter for low-cost household drinking water treatment. Physics and Chemistry of the Earth, Parts A/B/C. 34(1), pp. 36–42.

Harrison, C. J., Le Gouellec, Y. A., Cheng, R. C. and Childress, A. E., 2007. Bench-Scale Testing of Nanofiltration for Seawater Desalination. Journal of Environmental Engineering. 133(11), pp. 1004–1014.

Haynes, W. M., 2014. CRC Handbook of Chemistry and Physics, 95th Edition.

He, D., Jones, A. M., Garg, S., Pham, A. N. and Waite, T. D., 2011. Silver Nanoparticle−Reactive Oxygen Species Interactions: Application of a Charging−Discharging Model. The Journal of Physical Chemistry C. 115(13), pp. 5461–5468.

Heeb, M. B., Criquet, J., Zimmermann-Steffens, S. G. and von Gunten, U., 2014. Oxidative treatment of bromide-containing waters: formation of bromine and its reactions with inorganic and organic compounds--a critical review. Water research. 48, pp. 15–42.

Heidarpour, F., Wan Ab Karim Ghani, W. A., Fakhru'l-Razi, A., Sobri, S., Heydarpour, V., Zargar, M. and Mozafari, M. R., 2011. Complete removal of pathogenic bacteria from drinking water using nano silver-coated cylindrical polypropylene filters. Clean Technologies and Environmental Policy. 13(3), pp. 499–507.

Henglein, A. and Lilie, J., 1981. Storage of electrons in aqueous solution: the rates of chemical charging and discharging the colloidal silver microelectrode. Journal of the American Chemical Society. 103(5), pp. 1059–1066.

Ho, P. C. and Kraus, K. A., 1981. Adsorption on inorganic materials—VIII: Adsorption of iodide on AgCl-filled carbon. Journal of Inorganic and Nuclear Chemistry. 43(3), pp. 583–587.

Hoskins, J. A. Y. S., Karanfil, T., Carolina, S. and Serkiz, S. M., 2002. Removal and Sequestration of Iodide Using Silver-Impregnated Activated Carbon. 36(4), pp. 784–789.

Hoskins, J. S., Karanfi, T. and Serkiz, S. M., 2002. Removal and Sequestration of Iodide Using Silver-Impregnated Activated Carbon.

Hoskins, J. S., Karanfil, T. and Serkiz, S. M., 2002. Removal and Sequestration of Iodide Using Silver-Impregnated Activated Carbon. Environmental Science & Technology. 36(4), pp. 784–789.

Hsu, S. and Singer, P. C., 2010. Removal of bromide and natural organic matter by anion exchange. Water research. 44(7), pp. 2133–40.

Hua, G. and Reckhow, D. A., 2013. Effect of pre-ozonation on the formation and speciation of DBPs. Water Research. 47(13), pp. 4322–4330.

Huang, H.-I., Shih, H.-Y., Lee, C.-M., Yang, T. C., Lay, J.-J. and Lin, Y. E., 2008.

In vitro efficacy of copper and silver ions in eradicating Pseudomonas aeruginosa, Stenotrophomonas maltophilia and Acinetobacter baumannii: Implications for on-site disinfection for hospital infection control. Water Research. 42(1–2), pp. 73–80.

Hwang, M. G., Katayama, H. and Ohgaki, S., 2007. Inactivation of Legionella pneumophila and Pseudomonas aeruginosa: Evaluation of the bactericidal ability of silver cations. Water Research. 41(18), pp. 4097–4104.

Hyung, H. and Kim, J.-H., 2008. Natural Organic Matter (NOM) Adsorption to Multi-Walled Carbon Nanotubes: Effect of NOM Characteristics and Water Quality Parameters. Environmental Science & Technology. 42(12), pp. 4416–4421.

Jain, P. and Pradeep, T., 2005. Potential of silver nanoparticle-coated polyurethane foam as an antibacterial water filter. Biotechnology and Bioengineering. 90(1), pp. 59–63.

Jiang, Y., Goodwill, J. E., Tobiason, J. E. and Reckhow, D. A., 2015. Effect of Different Solutes, Natural Organic Matter, and Particulate Fe(III) on Ferrate(VI) Decomposition in Aqueous Solutions. Environmental Science & Technology. 49(5), pp. 2841–2848.

Jiang, Y., Goodwill, J. E., Tobiason, J. E. and Reckhow, D. A., 2016. Bromide oxidation by ferrate(VI): The formation of active bromine and bromate. Water Research. 96, pp. 188–197.

Jiang, Y., Goodwill, J. E., Tobiason, J. E. and Reckhow, D. A., 2016. Impacts of ferrate oxidation on natural organic matter and disinfection byproduct precursors. Water Research. 96, pp. 114–125.

Jones, A. M., Garg, S., He, D., Pham, A. N. and Waite, T. D., 2011. Superoxide-Mediated Formation and Charging of Silver Nanoparticles. Environmental Science & Technology. 45(4), pp. 1428–1434.

Karanfil, T., Kitis, M., And, J. E. K. and Wigton, A., 1999. Role of Granular Activated Carbon Surface Chemistry on the Adsorption of Organic

Compounds. 2. Natural Organic Matter. Environmental Science & Technology. 33(18), pp. 3225–3233.

Karanfil, T., Moro, E. C. and Serkiz, S. M., 2005. Development and Testing of a Silver Chloride-Impregnated Activated Carbon for Aqueous Removal and Sequestration of Iodide. Environmental Technology. 26(11), pp. 1255–1262.

Katz, W. E., 1982. Desalination by ED and EDR—state-of-the-art in 1981. Desalination. 42(2), pp. 129–139.

Khan, S., Wintgens, T., Sherman, P., Zaricky, J. and Schäfer, A., 2005. A performance comparison of individual and combined treatment modules for water recycling. Environmental Progress. 24(4), pp. 383–391.

Kilduff, J. E., Karanfil, T. and Weber, W. J., 1996. Competitive Interactions among Components of Humic Acids in Granular Activated Carbon Adsorption Systems: Effects of Solution Chemistry. Environmental Science & Technology. 30(4), pp. 1344–1351.

Kimbrough, D. E. and Suffet, I. ., 2002. Electrochemical removal of bromide and reduction of THM formation potential in drinking water. Water Research. 36(19), pp. 4902–4906.

Krasner, S. W., Weinberg, H. S., Richardson, S. D., Pastor, S. J., Chinn, R., Sclimenti, M. J., Onstad, G. D. and Thruston, A. D., 2006. Occurrence of a New Generation of Disinfection Byproducts †. Environmental Science & Technology. 40(23), pp. 7175–7185.

Kristiana, I., Joll, C. and Heitz, A., 2011. Powdered activated carbon coupled with enhanced coagulation for natural organic matter removal and disinfection by-product control: application in a Western Australian water treatment plant. Chemosphere. 83(5), pp. 661–7.

Kumar, K. and Margerum, D. W., 1987. Kinetics and mechanism of general-acid-assisted oxidation of bromide by hypochlorite and hypochlorous acid. Inorganic Chemistry. 26(16), pp. 2706–2711.

Kumar, R. and Münstedt, H., 2005. Silver ion release from antimicrobial polyamide/silver composites. Biomaterials. 26(14), pp. 2081–2088.

Łakomska, S. and Wiśniewski, J., 2013. Removal of bromide ions from an aqueous solution by Donnan dialysis with anion-exchange membranes. Desalination and Water Treatment. 51(7–9), pp. 1705–1711.

Landeen, L. K., Yahya, M. T., Kutz, S. M. and Gerba, C. P., 1989. Microbiological Evaluation of Copper : Silver Disinfection Units for Use in Swimming Pools. Water Science and Technology. 21(3), pp. 267–270.

Langsa, M., Heitz, A., Joll, C. A., von Gunten, U. and Allard, S., 2017. Mechanistic Aspects of the Formation of Adsorbable Organic Bromine during Chlorination of Bromide-containing Synthetic Waters. Environmental Science & Technology. 51(9), pp. 5146–5155.

Laurent Delannoy, Hassan, N. El, Andrea Musi, Nga Nguyen Le To, Jean-Marc Krafft, A. and Louis, C., 2006. Preparation of Supported Gold Nanoparticles by a Modified Incipient Wetness Impregnation Method.

Levenspiel, O., 1999. Chemical Reaction Engineering, 668. John Wiley & Sons, Inc., New York, USA.

Li, L., Sun, J., Li, X., Zhang, Y., Wang, Z., Wang, C., Dai, J. and Wang, Q., 2012. Controllable synthesis of monodispersed silver nanoparticles as standards for quantitative assessment of their cytotoxicity. Biomaterials. 33(6), pp. 1714–1721.

Li, Q., 2003. Pore blockage effect of NOM on atrazine adsorption kinetics of PAC: the roles of PAC pore size distribution and NOM molecular weight. Water Research. 37(20), pp. 4863–4872.

Lin, S., Huang, R., Cheng, Y., Liu, J., Lau, B. L. T. and Wiesner, M. R., 2013. Silver nanoparticle-alginate composite beads for point-of-use drinking water disinfection. Water Research. 47(12), pp. 3959–3965.

Liu, F., Wang, S., Fan, J. and Ma, G., 2012. Adsorption of Natural Organic Matter

Surrogates from Aqueous Solution by Multiwalled Carbon Nanotubes. The Journal of Physical Chemistry C. 116(49), pp. 25783–25789.

Liu, J. and Hurt, R. H., 2010. Ion Release Kinetics and Particle Persistence in Aqueous Nano-Silver Colloids. Environmental Science & Technology. 44(6), pp. 2169–2175.

Liu, J. and Hurt, R. H., 2010. Ion release kinetics and particle persistence in aqueous nano-silver colloids. Environmental science & technology. 44(6), pp. 2169–75.

Loo, S.-L., Fane, A. G., Lim, T.-T., Krantz, W. B., Liang, Y.-N., Liu, X. and Hu, X., 2013. Superabsorbent Cryogels Decorated with Silver Nanoparticles as a Novel Water Technology for Point-of-Use Disinfection. Environmental Science & Technology. 47(16), pp. 9363–9371.

Louie, S. M., Tilton, R. D. and Lowry, G. V., 2013. Effects of Molecular Weight Distribution and Chemical Properties of Natural Organic Matter on Gold Nanoparticle Aggregation. Environmental Science & Technology. 47(9), pp. 4245–4254.

Lv, L., Wang, Y., Wei, M. and Cheng, J., 2008. Bromide ion removal from contaminated water by calcined and uncalcined MgAl-CO3 layered double hydroxides. Journal of hazardous materials. 152(3), pp. 1130–7.

Lv, Y., Liu, H., Wang, Z., Liu, S., Hao, L., Sang, Y., Liu, D., Wang, J. and Boughton, R. I., 2009. Silver nanoparticle-decorated porous ceramic composite for water treatment. Journal of Membrane Science. 331(1–2), pp. 50–56.

Magazinovic, R. S., Nicholson, B. C., Mulcahy, D. E. and Davey, D. E., 2004. Bromide levels in natural waters: its relationship to levels of both chloride and total dissolved solids and the implications for water treatment. Chemosphere. 57(4), pp. 329–335.

Manceau, A. and Nagy, K. L., 2012. Quantitative analysis of sulfur functional groups in natural organic matter by XANES spectroscopy. Geochimica et Cosmochimica Acta. 99, pp. 206–223.

Matilainen, A. and Sillanpää, M., 2010. Removal of natural organic matter from drinking water by advanced oxidation processes. Chemosphere. 80(4), pp. 351–65.

Matilainen, A., Vepsäläinen, M. and Sillanpää, M., 2010. Natural organic matter removal by coagulation during drinking water treatment: a review. Advances in colloid and interface science. 159(2), pp. 189–97.

McDonald, S., Joll, C. A., Lethorn, A., Loi, C. and Heitz, A., 2013. Drinking water: the problem of chlorinous odours. Journal of Water Supply: Research and Technology-AQUA. 62(2), p. 86.

McKnight, D. M. and Aiken, G. R., 1998. Sources and age of aquatic humus. In Aquatic humic substances, pp. 9-39. Springer Berlin Heidelberg.

Miaomiao Zhang, Li, C., Mark M. Benjamin, and and Chang, Y., 2003. Fouling and Natural Organic Matter Removal in Adsorbent/Membrane Systems for Drinking Water Treatment.

Morones, J. R., Elechiguerra, J. L., Camacho, A., Holt, K., Kouri, J. B., Ramírez, J. T. and Yacaman, M. J., 2005. The bactericidal effect of silver nanoparticles. Nanotechnology. 16(10), pp. 2346–2353.

Moslemi, M., Davies, S. H. and Masten, S. J., 2012. Rejection of Bromide and Bromate Ions by a Ceramic Membrane. Environmental engineering science. 29(12), pp. 1092–1096.

Mpenyana-Monyatsi, L., Mthombeni, N. H., Onyango, M. S. and Momba, M. N. B., 2012. Cost-Effective Filter Materials Coated with Silver Nanoparticles for the Removal of Pathogenic Bacteria in Groundwater. International Journal of Environmental Research and Public Health. 9(12), pp. 244–271.

Nangmenyi, G., Xao, W., Mehrabi, S., Mintz, E. and Economy, J., 2009. Bactericidal activity of Ag nanoparticle-impregnated fibreglass for water disinfection. Journal of Water and Health. 7(4).

Nawaz, M., Han, M. Y., Kim, T., Manzoor, U. and Amin, M. T., 2012. Silver

disinfection of Pseudomonas aeruginosa and E. coli in rooftop harvested rainwater for potable purposes. Science of The Total Environment. 431, pp. 20–25.

Newcombe, G., 1997. Influence of characterised natural organic material on activated carbon adsorption: II. Effect on pore volume distribution and adsorption of 2-methylisoborneol. Water Research. 31(5), pp. 1065–1073.

Newcombe, G., 1999. Charge vs. porosity - Some influences on the adsorption of natural organic matter (NOM) by activated carbon. Water Science and Technology. 40(9), pp. 191–198.

Newcombe, G. and Drikas, M., 1997. Adsorption of NOM onto activated carbon: Electrostatic and non-electrostatic effects. Carbon. 35(9), pp. 1239–1250.

O'Loughlin, E. and Chin, Y.-P., 2001. Effect of detector wavelength on the determination of the molecular weight of humic substances by high-pressure size exclusion chromatography. Water Research. 35(1), pp. 333–338.

Ortiz-Ibarra, H., Casillas, N., Soto, V., Barcena-Soto, M., Torres-Vitela, R., de la Cruz, W. and Gómez-Salazar, S., 2007. Surface characterization of electrodeposited silver on activated carbon for bactericidal purposes. Journal of colloid and interface science. 314(2), pp. 562–71.

Oyanedel-Craver, V. A. and Smith, J. A., 2008. Sustainable Colloidal-Silver-Impregnated Ceramic Filter for Point-of-Use Water Treatment. Environmental Science & Technology. 42(3), pp. 927–933.

Pan, Y. and Zhang, X., 2013. Four Groups of New Aromatic Halogenated Disinfection Byproducts: Effect of Bromide Concentration on Their Formation and Speciation in Chlorinated Drinking Water. Environmental Science & Technology. 47(3), pp. 1265–1273.

Pathak, S. P. and Gopal, K., 2012. Evaluation of bactericidal efficacy of silver ions on Escherichia coli for drinking water disinfection. Environmental Science and Pollution Research. 19(6), pp. 2285–2290.

Pelekani, C. and Snoeyink, V. ., 1999. Competitive adsorption in natural water: role of activated carbon pore size. Water Research. 33(5), pp. 1209–1219.

Plewa, M. J., Kargalioglu, Y., Vankerk, D., Minear, R. A. and Wagner, E. D., 2002. Mammalian cell cytotoxicity and genotoxicity analysis of drinking water disinfection by-products. Environmental and Molecular Mutagenesis. 40(2), pp. 134–142.

Polo, A. M. S., I., V.-G., M., S.-P., U., von G., J.J., L.-P. and J., R.-U., 2016. Halide removal from aqueous solution by novel silver-polymeric materials. Science of The Total Environment. 573, pp. 1125–1131.

Putra, E. K., Pranowo, R., Sunarso, J., Indraswati, N. and Ismadji, S., 2009. Performance of activated carbon and bentonite for adsorption of amoxicillin from wastewater: Mechanisms, isotherms and kinetics. Water Research. 43(9), pp. 2419–2430.

Qi, S., Schideman, L. C. and Boyer, T. H., 2012. Determining Minimum Ion Exchange Resin Usage for NOM Removal. Journal of Environmental Engineering. 138(10), pp. 1058–1066.

Qian, Q., Shao, S., Yan, F. and Yuan, G., 2008. Direct removal of trace ionic iodide from acetic acid via porous carbon spheres. Journal of Colloid and Interface Science. 328(2), pp. 257–262.

Ren, D. and Smith, J. A., 2013. Retention and Transport of Silver Nanoparticles in a Ceramic Porous Medium Used for Point-of-Use Water Treatment. Environmental Science & Technology. 47(8), pp. 3825–3832.

Richardson, S. D., Plewa, M. J., Wagner, E. D., Schoeny, R. and DeMarini, D. M., 2007. Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research. Mutation Research/Reviews in Mutation Research. 636(1), pp. 178–242.

Richardson, S. D., Thruston, A. D., Caughran, T. V., Chen, P. H., Collette, T. W. and Floyd, T. L., 1999. Identification of New Drinking Water Disinfection Byproducts Formed in the Presence of Bromide. Environmental Science &

Technology. 33(19), pp. 3378–3383.

Sakuma, M., Matsushita, T., Matsui, Y., Aki, T., Isaka, M. and Shirasaki, N., 2015. Mechanisms of trichloramine removal with activated carbon: Stoichiometric analysis with isotopically labeled trichloramine and theoretical analysis with a diffusion-reaction model. Water Research. 68, pp. 839–848.

Sánchez-Polo, M., Rivera-Utrilla, J. and von Gunten, U., 2006. Metal-doped carbon aerogels as catalysts during ozonation processes in aqueous solutions. Water research. 40(18), pp. 3375–84.

Sánchez-Polo, M., Rivera-Utrilla, J. and von Gunten, U., 2007. Bromide and iodide removal from waters under dynamic conditions by Ag-doped aerogels. Journal of colloid and interface science. 306(1), pp. 183–6.

Sánchez-Polo, M., Rivera-Utrilla, J., Salhi, E. and von Gunten, U., 2006. Removal of bromide and iodide anions from drinking water by silver-activated carbon aerogels. Journal of Colloid and Interface Science. 300(1), pp. 437–441.

Sánchez-Polo, M., Rivera-Utrilla, J., Salhi, E. and von Gunten, U., 2006. Removal of bromide and iodide anions from drinking water by silver-activated carbon aerogels. Journal of colloid and interface science. 300(1), pp. 437–41.

Sánchez-Polo, M., Rivera-Utrilla, J., Salhi, E. and von Gunten, U., 2007. Ag-doped carbon aerogels for removing halide ions in water treatment. Water research. 41(5), pp. 1031–7.

Sata, T., 2000. Studies on anion exchange membranes having permselectivity for specific anions in electrodialysis - effect of hydrophilicity of anion exchange membranes on permselectivity of anions. Journal of Membrane Science. 167(1), pp. 1–31.

Sedlak, D. L. and von Gunten, U., 2011. Chemistry. The chlorine dilemma. Science (New York, N.Y.). 331(6013), pp. 42–3.

Settimio, L., McLaughlin, M. J., Kirby, J. K., Langdon, K. A., Janik, L. and Smith, S., 2015. Complexation of silver and dissolved organic matter in soil water

extracts. Environmental Pollution. 199, pp. 174–184.

Sharma, V. K., Zboril, R. and McDonald, T. J., 2014. Formation and toxicity of brominated disinfection byproducts during chlorination and chloramination of water: A review. Journal of Environmental Science and Health, Part B. 49(3), pp. 212–228.

Shoeib, T., Siu, K. W. M. and Hopkinson, A. C., 2002. Silver Ion Binding Energies of Amino Acids: Use of Theory to Assess the Validity of Experimental Silver Ion Basicities Obtained from the Kinetic Method. The Journal of Physical Chemistry A. 106(25), pp. 6121–6128.

Silvestry-Rodriguez, N., Bright, K. R., Slack, D. C., Uhlmann, D. R. and Gerba, C. P., 2008. Silver as a residual disinfectant to prevent biofilm formation in water distribution systems. Applied and environmental microbiology. 74(5), pp. 1639–41.

Silvestry-Rodriguez, N., Bright, K. R., Uhlmann, D. R., Slack, D. C. and Gerba, C. P., 2007. Inactivation of *Pseudomonas aeruginosa* and *Aeromonas hydrophila* by silver in tap water. Journal of Environmental Science and Health, Part A. 42(11), pp. 1579–1584.

Singer, P. C., 1999. Humic substances as precursors for potentially harmful disinfection by-products. Water Science and Technology. 40(9), pp. 25–30.

Smith, R., Martell, A. and Motekaitis, R., 1998. NIST critically selected stability constants of metal complexes database.

Sondi, I. and Salopek-Sondi, B., 2004. Silver nanoparticles as antimicrobial agent: a case study on E. coli as a model for Gram-negative bacteria. Journal of Colloid and Interface Science. 275(1), pp. 177–182.

Strathmann, H., 2010. Electrodialysis, a mature technology with a multitude of new applications. Desalination. 264(3), pp. 268–288.

Stumm, W., 1992. Chemistry of the solid-water interface: processes at the mineral-water and particle-water interface in natural systems, 428. John Wiley & Sons,

Inc., New York, USA.

Stumm, W. and Morgan, J. J., 1996. Aquatic chemistry: chemical equilibria and rates in natural waters, 1022. John Wiley & Sons, Inc., New York, USA.

Tan, J., Allard, S., Gruchlik, Y., McDonald, S., Joll, C. A. and Heitz, A., 2016. Impact of bromide on halogen incorporation into organic moieties in chlorinated drinking water treatment and distribution systems. Science of The Total Environment. 541, pp. 1572–1580.

Tan, J., Allard, S., Gruchlik, Y., McDonald, S., Joll, C. A. and Heitz, A., 2016. Impact of bromide on halogen incorporation into organic moieties in chlorinated drinking water treatment and distribution systems. Science of The Total Environment. 541, pp. 1572–1580.

Valero, F. and Arbós, R., 2010. Desalination of brackish river water using Electrodialysis Reversal (EDR). Desalination. 253(1–3), pp. 170–174.

Vilgé-Ritter, A., Masion, A., Boulangé, T., Danielle Rybacki, A. and Bottero, J.-Y., 1999. Removal of Natural Organic Matter by Coagulation-Flocculation: A Pyrolysis-GC-MS Study. Environmental Science & Technology. 33(17), pp. 3027–3032.

Watson, K., Farré, M. J. and Knight, N., 2012. Strategies for the removal of halides from drinking water sources, and their applicability in disinfection by-product minimisation: A critical review. Journal of Environmental Management. 110, pp. 276–298.

Watson, K., Farré, M. J. and Knight, N., 2016. Comparing a silver-impregnated activated carbon with an unmodified activated carbon for disinfection by-product minimisation and precursor removal. Science of the Total Environment. 542, pp. 672–684.

Weber, W. and Morris, J., 1963. Kinetics of adsorption on carbon from solution. Journal of the Sanitary Engineering Division. 89(2), pp. 31–60.

Welgemoed, T. J. and Schutte, C. F., 2005. Capacitive Deionization Technology™:

An alternative desalination solution. Desalination. 183(1–3), pp. 327–340.

Wiśniewski, J. A. and Kliber, S., 2011. Removal of harmful anions from water in the anion-exchange membrane process. Desalination and Water Treatment. 34(1–3), pp. 13–18.

Xiu, Z.-M., Ma, J. and Alvarez, P. J. J., 2011. Differential Effect of Common Ligands and Molecular Oxygen on Antimicrobial Activity of Silver Nanoparticles versus Silver Ions. Environmental Science & Technology. 45(20), pp. 9003–9008.

Yang, X., Guo, W., Zhang, X., Chen, F., Ye, T. and Liu, W., 2013. Formation of disinfection by-products after pre-oxidation with chlorine dioxide or ferrate. Water Research. 47(15), pp. 5856–5864.

Yang, X., Jiang, C., Hsu-Kim, H., Badireddy, A. R., Dykstra, M., Wiesner, M., Hinton, D. E. and Meyer, J. N., 2014. Silver Nanoparticle Behavior, Uptake, and Toxicity in Caenorhabditis elegans : Effects of Natural Organic Matter. Environmental Science & Technology. 48(6), pp. 3486–3495.

Yang, Y., Komaki, Y., Kimura, S. Y., Hu, H.-Y., Wagner, E. D., Mariñas, B. J. and Plewa, M. J., 2014. Toxic Impact of Bromide and Iodide on Drinking Water Disinfected with Chlorine or Chloramines. Environmental Science & Technology. 48(20), pp. 12362–12369.

Yoo, J., Shim, T., Hur, J. and Jung, J., 2016. Role of polarity fractions of effluent organic matter in binding and toxicity of silver and copper. Journal of Hazardous Materials. 317, pp. 344–351.

Zhang, H., Smith, J. A. and Oyanedel-Craver, V., 2012. The effect of natural water conditions on the anti-bacterial performance and stability of silver nanoparticles capped with different polymers. Water Research. 46(3), pp. 691–699.

Zhao, X., Salhi, E., Liu, H., Ma, J. and von Gunten, U., 2016. Kinetic and Mechanistic Aspects of the Reactions of Iodide and Hypoiodous Acid with Permanganate: Oxidation and Disproportionation. Environmental Science & Technology. 50(8), pp. 4358–4365.

Zhou, J., Cheng, Y., Yu, J. and Liu, G., 2011. Hierarchically porous calcined lithium/aluminum layered double hydroxides: Facile synthesis and enhanced adsorption towards fluoride in water. Journal of Materials Chemistry. 21(48), pp. 19353–19361.

Zularisam, A. W., Ismail, A. F. and Salim, R., 2006. Behaviours of natural organic matter in membrane filtration for surface water treatment - a review. Desalination. 194(1–3), pp. 211–231.